ARENE RUTHENIUM HYDRIDO COMPLEXES

AND THEIR CYCLOMETALLATED DERIVATIVES

by

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Abbreviations

bipy	2,2'-bipyridine
br	broad
Carb	2-phenyl-1,2-dicarba-closo-dodecaboranyl
cod	1,5-cyclooctadiene
Cy	cyclohexyl
d	doublet
DBN	1,5-diazabicyclo[4.3.0]non-5-ene
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
dmso	dimethylsulphoxide
dmpe	1,2-bis(dimethylphosphino)ethane
dppe	1,2-bis(diphenylphosphino)ethane
o-phen	o-phenanthroline
o-Tol	ortho-tolyl
q	quartet
qu	quintet
Red-Al	$Na[AlH_2(OCH_2CH_2OCH_3)_2]$
s	singlet
sh	shoulder
t	triplet
tbe	t-butylethylene, 3,3-dimethyl-1-butene
THF	tetrahydrofuran
tmen	tetramethylethylenediamine; N,N,N',N'-tetramethyl-1,2-diaminoethane
TMS	tetramethylsilane

ABSTRACT

A large number of the hydrides $RuHCl(\eta^6\text{-}C_6Me_6)L$ {L = PR_3, $AsPh_3$, $SbPh_3$} have been prepared. There was hitherto no general route to these hydrido complexes, but four useful methods for their synthesis have been found: by heating $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ with an excess of ligand and sodium carbonate in 2-propanol; by heating $RuCl_2(\eta^6\text{-}C_6Me_6)L$ with sodium carbonate in 2-propanol; or by the displacement of $AsPh_3$ or $SbPh_3$ from $RuHCl(\eta^6\text{-}C_6Me_6)(EPh_3)$ {E = As, Sb} by a tertiary phosphine. Heating of $RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_2\underline{o}\text{-Tol})$ with sodium carbonate in 2-propanol yields $\overline{RuCl(\underline{o}\text{-}CH_2C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$.

Treatment of the complexes $RuHCl(\eta^6\text{-}C_6Me_6)(PR_3)$ {PR_3 = $P(\underline{p}\text{-}C_6H_4CH_3)_3$, $P(\underline{p}\text{-}C_6H_4F)_3$, PBu^tPh_2, PPh_2Pr^i, $PEtPh_2$, PPh_2Pr^n, $PPh_2\underline{o}$-Tol, PBu^t_2Me, PBu^t_2Et, $PBu^t_2Pr^n$, PPr^i_3, PBu^tMe_2, $PMePh_2$} with methyllithium generally leads to the cyclometallated hydrides $\overline{RuH(C\sim PR_2)}(\eta^6\text{-}C_6Me_6)$. When PR_3 = PMe_2Ph, PMe_3, cyclometallation is not observed. Treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PR_3)$ with phenyllithium gives $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PR_3)$ for small tertiary phosphine ligands, and a mixture of cyclometallated hydrides and hydridophenyls for more sterically demanding phosphine ligands. The dihydrides $RuH_2(\eta^6\text{-}C_6Me_6)(PR_3)$ are often by-products of the reactions of $RuHCl(\eta^6\text{-}C_6Me_6)(PR_3)$ with methyllithium and phenyllithium. When the tertiary phosphine bears two different substituents, the preferred site of metallation depends on the nature of the substituents.

The alkylation of $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tPh_2)$ with methyllithium below room temperature forms exclusively $\overline{RuH(CH_2CMe_2PPh_2)}(\eta^6\text{-}C_6Me_6)$ [31], which isomerizes in a first order manner to $\overline{RuH(\underline{o}\text{-}C_6H_4PBu^tPh)}(\eta^6\text{-}C_6Me_6)$ [32] at 50°. This is the first observed instance

of isomerization between two different sites of cyclometallation in a phosphine ligand.

The cyclometallation of tertiary phosphine ligands bearing two different substituents is usually competitive, giving rise to mixtures of products, often including diastereoisomers. The kinetically preferred site of metallation depends on the phosphine ligand. These metallations are usually reversible, forming the thermodynamically preferred isomers by a first order process. For the compounds obtained by treating $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2R)$ {R = Bu^t, Pr^n, Pr^i} with methyllithium, the rate of isomerization of the kinetically preferred isomers follows the order ortho-aryl metallated < t-butyl metallated < isopropyl metallated groups. The thermodynamic preference for the site of metallation depends on the nature of the chelate ring formed, with the general preference being four-membered alkyl rings < four-membered aryl rings < five-membered rings. The kinetic preference is usually independent of the thermodynamic preference. In no case has any phosphine alkyl substituent been metallated at the α carbon atom.

The cyclometallation of PBu^tMe_2 in the complex $\overline{RuH(CH_2CMe_2PMe_2)}(\eta^6\text{-}C_6Me_6)$ [48] is reversible. The reaction of [48] with neat benzene to form $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ is pseudo-first order and irreversible, but attempts to trap the intermediate $Ru(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ with π-acceptor ligands have been unsuccessful.

The factors controlling the selectivity of intramolecular and intermolecular C-H bond oxidative addition in the system $Ru(\eta^6\text{-}C_6Me_6)(PR_3)$ are the steric environment of the metal, ruthenium-carbon bond strengths and ring strain.

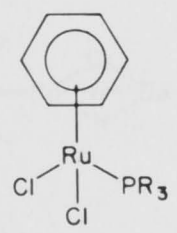
CHAPTER 1

INTRODUCTION

Organometallic complexes are now well known for their ability to trap a variety of short-lived and unstable organic molecules, as catalysts for a wide range of processes, and for activating otherwise unreactive sites to a wide variety of reagents. Arene ruthenium complexes have recently been found to perform all three of these functions.

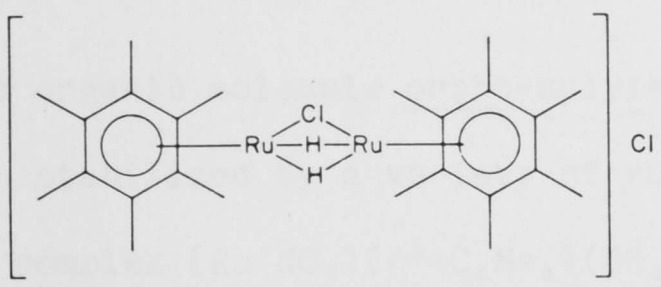
The first arene ruthenium complexes were reported by Fischer and Böttcher in 1957.[64] The bis(arene) complexes $[Ru(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)_2]^{2+}$ and $[Ru(\eta^6\text{-}C_6H_6)_2]^{2+}$ were prepared by heating $RuCl_3$, $AlCl_3$ and aluminium powder in arene solvent under slight pressure for several hours.

The first mono(arene) ruthenium complexes were described in 1967 by Winkhaus and Singer.[186] They found that refluxing of 1,3-cyclohexadiene with ruthenium trichloride in ethanol formed a benzene complex which they formulated as the polymeric $[RuCl_2(\eta^4\text{-}C_6H_6)]_n$. Treatment of the "polymer" with tri-n-butylphosphine formed a derivative which they formulated as the dimer $[RuCl_2(\eta^4\text{-}C_6H_6)(PBu^n_3)]_2$. Zelonka and Baird found, on the basis of



spectroscopic and molecular weight data, that these complexes in fact contained η^6-arene ligands, and were dimeric and monomeric respectively.[190] This was confirmed by X-ray crystal structures of $RuCl_2(\eta^6\text{-}C_6H_6)(PMePh_2)$ [1] and $RuCl_2(\eta^6\text{-}\underline{p}\text{-}MeC_6H_4Pr^i)(PMePh_2)$, which showed that the phosphine complexes had a "piano-stool" type of structure.[23] Since that time, the chemistry of areneruthenium compounds has been extensively developed.

Many areneruthenium compounds are hydrogenation catalysts. The complexes $[RuCl_2(\eta^6\text{-arene})]_2$ {arene = C_6H_6, 1,3,5-$C_6H_3Me_3$, 1,3,5-$C_6H_3Ph_3$}[90,103,143] and $RuCl_2(\eta^6\text{-}C_6H_6)(DMSO)$[143] were found to be catalyst precursors for hydrogenation of alkenes, but not benzene. The zero-valent ruthenium complex $Ru(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_6)$,[65,99] was found to be catalytically active for arene hydrogenation.[107] The products were cyclohexanes together with some cyclohexenes. Addition of trimethylaluminium or dimethylaluminium chloride significantly enhanced the rate of arene hydrogenation and suppressed the formation of the cyclohexenes.[58] The complex $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ was found to be an active catalyst for arene hydrogenation and for transfer hydrogenation from 1-phenylethanol to a variety of alkenes.[16] The catalytic activity of $\{[Ru(\eta^6\text{-}C_6Me_6)]_2(\mu\text{-}H)_2(\mu\text{-}Cl)\}Cl$ [2] towards arene hydrogenation was far greater than that of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$. A wide variety of arenes were rapidly hydrogenated to

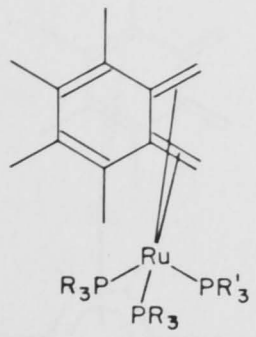


[2]

cyclohexanes in the presence of [2], in many cases, without hydrogenolysis of heteroatom carbon bonds.[17] Unfortunately, the synthesis of [2] has proven to be irreproducible, but two related species, $\{[Ru(\eta^6\text{-}C_6Me_6)]_2(\mu\text{-}H)(\mu\text{-}Cl)_2\}Cl$ and $\{[Ru(\eta^6\text{-}C_6Me_6)]_2(\mu\text{-}H)_3\}Cl$ were also found to catalyse the hydrogenation of benzene to cyclohexane, although they were less active than either [2] or $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$.[12] The analogous iridium and rhodium ($\eta^5\text{-}C_5Me_5$) complexes have been reported to be alkene[70] and arene[155] hydrogenation catalysts. More recently, the hydrogenation of alkenes in the presence of the catalysts $Ru(\eta^6\text{-arene})(\eta^4\text{-COD})$ {arene = C_6H_6, 1,4-$C_6H_4Me_2$, 1,3,5-$C_6H_3Me_3$} was reported.[150]

Arene ruthenium compounds also promote a number of stoichiometric reactions. The cyclotrimerization of alkynes to arenes was reported to be mediated by $Ru(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$ under ultraviolet irradiation. The product of this reaction was either $Ru(\eta\text{-}C_6H_6)(\eta\text{-arene})$ or $Ru(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_6)$ {depending on the alkyne}, which was formed in low to moderate yield.[130] Benzene was selectively reduced to cyclohexene by hydride reduction of $[Ru(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}C_6H_6)]^{2+}$ and $[M(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_6)]^{2+}$ {M = Ir, Rh}, followed by protonation. When the protonation was carried out in benzene in the presence of a poorly co-ordinating counter-ion, the starting complexes were regenerated. Under these conditions the protonation was formally catalytic in the complex, but the number of turnovers was low.[84]

The unstable organic molecule ortho-xylylene and its derivatives have been stabilized by a variety of ruthenium complexes. Deprotonation of the complex $[Ru(NO_3)(\eta^6\text{-}C_6Me_6)(PR_3)_2]^+$ with a strong base in the presence of PR'_3 generated the zero-valent tetramethyl-ortho-xylylene complex $Ru[\eta^4\text{-}o\text{-}C_6(CH_2)_2Me_4](PR_3)_2(PR'_3)$ [3], in



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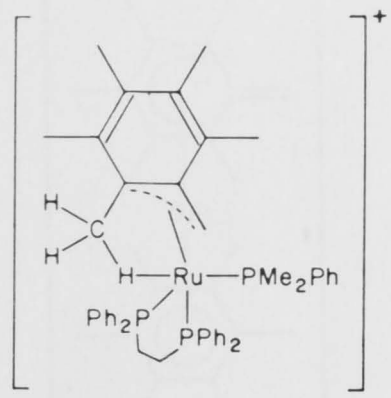
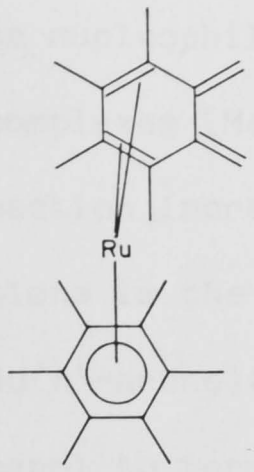


[4]

which the ruthenium is co-ordinated to the exocyclic diene group. The hexamethylbenzene ring was readily restored by protonation of the trimethylphosphite complex [3] {$PR_3 = PR'_3 = P[OMe]_3$}, forming {$Ru(\eta^6\text{-}C_6Me_6)(P[OMe]_3)_3\}^{2+}$, but monoprotonation to form the fluxional molecule [4] was the only result on treating [3] {$(PR_3)_2$ = dppe, PR'_3 = PMe_2Ph} with excess acid.[18] Deprotonation is a general reaction for complexes of this type: similar treatment of the analogous ortho-xylene and 1,2,4,5-tetramethylbenzene complexes formed the ortho-xylylene and 4,5-dimethyl-ortho-xylylene analogues of [3].[13]

The ortho-xylylene analogues of [3] were independently synthesized by treatment of $RuCl_2(PR_3)_4$ with o-$CH_3C_6H_4CH_2MgBr$ or o-$CH_3C_6H_4CH_2Li$(tmen). These reactions were believed to proceed via loss of ortho-xylene from a σ-alkyl intermediate $Ru(CH_2C_6H_4CH_3)_2(PR_3)_n$ {n = 3 or 4}. An X-ray crystal structure determination of $Ru[\eta^4\text{-}o\text{-}C_6H_4(CH_2)_2](PMe_2Ph)_3$ confirmed the η^4-exocyclic bonding mode of the xylylene ligand.[43] Deprotonation of the bis(arene) complex $[Ru(\eta^6\text{-}C_6Me_6)_2]^{2+}$ with $KOBu^t$ formed the ortho-xylylene complex $Ru[\eta^4\text{-}o\text{-}C_6(CH_2)_2Me_4](\eta^6\text{-}C_6Me_6)$ [5] in which the metal atom is bonded to the endocyclic diene functionality. The deprotonation was reversible and proceeded stepwise via the methylenecyclohexadienyl complex [6].[98]



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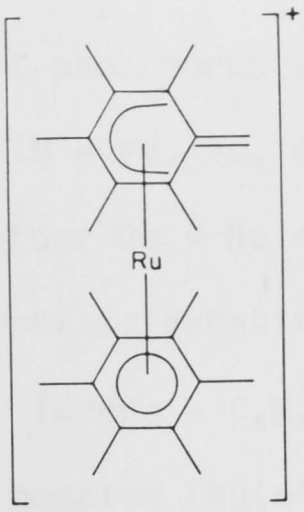


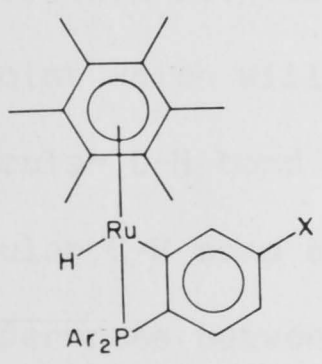
[6]

The arene ligands in cationic areneruthenium(II) complexes are activated towards attack by nucleophiles. The reaction between the bis(benzene) cation $[Ru(\eta^6\text{-}C_6H_6)_2]^{2+}$ and sodium borohydride formed the 1,3-cyclohexadiene complex $Ru(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$. The cyclohexadienyl cation $[Ru(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_6H_7)]^+$, formed by addition of one hydride ion to the dication, was not detected. It was also not possible to prepare $[Ru(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_6H_7)]^+$ by abstraction of hydride from $Ru(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$ using one equivalent of CPh_3^+. Phenyllithium attacked both rings of $[Ru(\eta^6\text{-}C_6H_6)_2]^{2+}$ to give bis(η^5-phenylcyclohexadienyl)-ruthenium(II).[110] When the reaction of $[Ru(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(\eta^6\text{-}C_6H_6)]^{2+}$ with sodium borohydride was carried out in water in place of THF the intermediate cyclohexadienyl complex $[Ru(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(\eta^5\text{-}C_6H_7)]^+$ was isolated.[156] The hexamethylbenzene complex $[Ru(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}C_6H_6)]^{2+}$ behaved analogously.[84] Both complexes were reduced to the cyclohexadiene complexes by addition of a hydridic reagent in THF.

Nucleophilic addition of $(C_6H_5)^-$ and H^- to the arene ring of $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]^+$,[173] of H^-, CN^- and OH^- to the co-ordinated arene of $[Ru(\eta^6\text{-}C_6H_6)L_2(PR_3)]^{2+}$ {L_2 = bipy, o-phen},[153] and of PR_3 to the arene ring of $[RuCl(\eta^6\text{-}C_6H_6)(PR'_3)(PR''_3)]^+$ [185] have been observed. Nucleophilic attack was always exo to the ring. A study of the

kinetics of the nucleophilic addition of phosphorus donors to the bis(benzene) complexes $[M(\eta^6\text{-}C_6H_6)_2]^{2+}$ {M = Fe, Ru, Os} showed that the rate of reaction increased in the order Os < Ru << Fe.[49] Related to these reactions is the facile nucleophilic substitution of the chloride in $[Ru(\eta^6\text{-arene})(\eta^6\text{-}C_6H_5Cl)]^{2+}$ {arene = C_6H_6, 1,3,5-$C_6H_3Me_3$, C_6Me_6} by methanol to form the anisole complex $[Ru(\eta^6\text{-arene})(\eta^6\text{-}C_6H_5OCH_3)]^{2+}$,[19] and of the chloride and fluoride in $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_5X)]^{+}$ {X = Cl, F} by OH^-, CH_3O^-, NH_2^-, PhS^- and piperidide.[141,173]

A number of areneruthenium compounds have been found to activate C-H bonds. Treatment of $RuCl_2(\eta^6\text{-}C_6Me_6)L$ with EtMgBr gave a series of ortho-metallated hydrides $\overline{RuH[(\underline{o}\text{-}C_6H_3\text{-}\underline{p}\text{-}X)PAr_2]}(\eta^6\text{-}C_6Me_6)$ [7] for L = triarylphosphine. When L = $P[OR]_3$, PBu^n_3, $PMePh_2$, a zero-valent ruthenium ethylene complex $Ru(\eta^6\text{-}C_6Me_6)(\eta^2\text{-}C_2H_4)L$ [8] was the sole product. Under similar conditions, the mesitylene analogue $RuCl_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PPh_3)$ gave a 1:1 mixture of $\overline{RuH(\underline{o}\text{-}C_6H_4PPh_2)}(\eta^6\text{-}C_6H_3Me_3)$ and $Ru(\eta^6\text{-}C_6H_3Me_3)(\eta^2\text{-}C_2H_4)(PPh_3)$, whilst the benzene analogue formed only the ethylene complex $Ru(\eta^6\text{-}C_6H_6)(\eta^2\text{-}C_2H_4)(PPh_3)$.[97] Similarly, treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ with methyllithium, phenyllithium or Red-Al $\{Na[AlH_2(OCH_2CH_2OCH_3)_2]\}$ formed $\overline{RuH(\underline{o}\text{-}C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$.[14,97] The cyclometallation reaction is believed to be an intramolecular C-H bond activation process.



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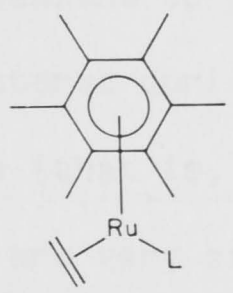

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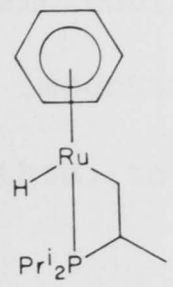


[9]

During the course of this work, a number of intermolecular C-H bond cleavages promoted by areneruthenium complexes were reported. Irradiation of the dihydride complexes $RuH_2(\eta^6\text{-}C_6H_6)(PPr^i_3)$ and $RuH_2(\eta^6\text{-}C_6Me_6)(PMe_3)$ in benzene gave the hydridophenyl complexes $RuH(C_6H_5)(\eta^6\text{-arene})(PR_3)$, in which the hydride and phenyl ligands were formed by cleaving a solvent C-H bond. Irradiation of $RuH_2(\eta^6\text{-}C_6H_6)(PPr^i_3)$ in cyclohexane induced a cyclometallation of the phosphine ligand to form $\overline{RuH(CH_2CHMePPr^i_2)}(\eta^6\text{-}C_6H_6)$ [9]. In benzene, [9] reacted to give $RuH(C_6H_5)(\eta^6\text{-}C_6H_6)(PPr^i_3)$ [10], which was formed by attack on the solvent.[124] The analogous secondary phosphine complex $RuH_2(\eta^6\text{-}C_6Me_6)(PHCy_2)$ reacted with benzene under irradiation to give $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PHCy_2)$. No P-H bond cleavage was observed.[138] These reactions parallel those of the isoelectronic pentamethylcyclopentadienyliridium and rhodium systems {see below}.

The reaction between [9] and benzene to give [10] illustrates an important point which will be encountered during this work, namely, that intramolecular C-H bond activation {that is, cyclometallation} and intermolecular C-H bond activation are very similar processes, and the energy differences between them are not necessarily large. This point is clearly emphasized by the observed equilibrium between $RhH(C_6H_5)(\eta^5\text{-}C_5Me_5)(PMe_2[CH_2Ph])$ and $\overline{RhH(\underline{o}\text{-}C_6H_4CH_2PMe_2)}(\eta^5\text{-}C_5Me_5)$ in

benzene solution.[112] Both intramolecular and intermolecular C-H bond scission have been found to be important processes for areneruthenium compounds. It is appropriate, then, to comment further on these processes.

Intramolecular and intermolecular C-H bond activation have been studied intensively in recent years. Several reviews on intermolecular C-H bond activation have appeared.[140,146,162,179] Reviews of cyclometallation reactions are numerous, but Bruce's review is notable for its scope.[32] Reviews on tertiary phosphine[144] and arsine[145] complexes are particularly relevant to this work. The activation of C-H bonds manifests itself in three ways: (a) H/D exchange, which involves intramolecular and intermolecular bond scission; (b) transfer dehydrogenation, which is by nature intermolecular; (c) stoichiometric cleavage of C-H bonds, which again can be either intramolecular or intermolecular.

Catalytic H/D exchange has been observed for a wide range of transition metal complexes. The first reported examples were for exchange of hydrogen for deuterium in a variety of alkanes[93,162] and arenes[91] catalysed by $[PtCl_4]^{2-}$ in highly acidic media. Exchange was believed to proceed by reversible oxidative addition of C-H bonds. The observation of a platinum(IV) methyl species in a reaction mixture obtained by heating methane with $[PtCl_4]^{2-}$ and $[PtCl_6]^{2-}$ in water supports this proposal.[126] Formation of intermediate π-complexes was also believed to be involved in H/D exchange in aromatic solvents catalysed by $[PtCl_4]^{2-}$.[91] Subsequently, a wide variety of organometallic, and, in particular, hydridic species have been found to catalyse H/D exchange. Polyhydride complexes of iridium, tantalum, niobium[7,122,123] and rhenium[77] catalysed H/D exchange between D_2 gas

or C_6D_6 and a wide variety of aromatic and aliphatic substrates. A number of hydride complexes of cobalt, rhodium, ruthenium[121,147] and rhenium,[189] as well as the binuclear platinum phosphine complexes $Pt_2Cl_4(PR_3)_2$[117] and the rhodium complex $Rh(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_2H_4)_2$,[159] incorporated deuterium into various sites of their ligands by exchanging hydrogen with deuterium from deuterated aromatic solvents. All of these H/D exchange processes were proposed to occur by oxidative addition/reductive elimination reactions of the exchanged C-H bonds.

The transfer dehydrogenation reaction is also a C-H bond activation process. It formally involves transfer of hydrogen from an alkane {or, in some instances, an alkene} to an unsaturated molecule. Only a few homogeneous catalytic systems are known. The polyhydride species IrH_5L_2 {L = PPr^i_3, $P[\underline{p}\text{-}C_6H_4F]_3$} and $RuH_4[P(\underline{p}\text{-}C_6H_4F)_3]_2$ catalysed the transfer of hydrogen from cyclooctane to 3,3-dimethyl-1-butene (tbe) to form cyclooctene and 3,3-dimethylbutane.[60] The acetone complex $\{IrH_2(CH_3COCH_3)_2[P(\underline{p}\text{-}C_6H_4F)_3]_2\}^+$ catalysed the dehydrogenation of cyclohexene to benzene in the presence of tbe.[39] Similarly, $[RhCl(cyclooctene)_2]_2$, when it was treated with two equivalents of phosphine, catalysed hydrogen transfer from 1,4-dioxane to cyclopentene, forming 1,4-dioxene and cyclopentane.[137] A number of complexes also catalysed the disproportionation of cyclohexadienes to cyclohexene and benzene,[131,139] and of cyclohexene to cyclohexane and benzene.[39]

Polyhydride complexes of iridium[39,53,54,55] and rhenium[8,9,10] reacted with various linear alkanes and cycloalkanes or cycloalkenes in the presence of hydrogen acceptors to form complexes bearing unsaturated ligands. For example, heating of $[IrH_2(CH_3COCH_3)_2(PPh_3)_2]^+$

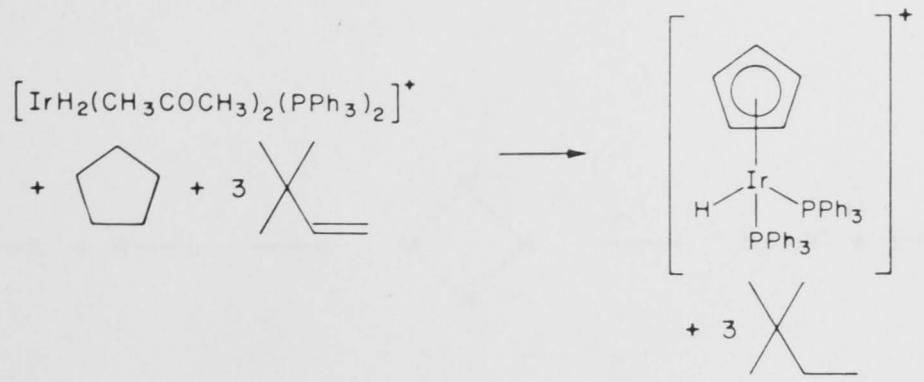


Figure 1-1

with cyclopentane and tbe formed $[IrH(\eta^5\text{-}C_5H_5)(PPh_3)_2]^+$ and 3,3-dimethylbutane {Figure1-1}.[53] All of the hydrogen transfer reactions were thought to involve cycles of alkene insertion, reductive elimination of the new alkyl C-H bond, oxidative addition of alkane {alkene} C-H bond and β-elimination.

Related ligand dehydrogenations were observed on treating $[IrCl(cyclooctene)_2]_2$ with tricyclohexylphosphine to form an iridium hydride complex, $IrH_2Cl[P(C_6H_9)Cy_2](PCy_3)$, containing a cyclohexenyldicyclohexylphosphine ligand.[104] The product apparently disproportionated on heating to form $IrH_2Cl(PCy_3)_2$ and $IrCl[P(C_6H_9)Cy_2](PCy_3)$.[89] Co-condensation of tungsten atoms with trimethylphosphine and cyclopentane or cyclopentene afforded a number of cyclopentadienyltungsten hydride complexes.[81] In both the iridium and tungsten systems, the metal acted as a hydrogen acceptor.

There are two mechanisms common to intramolecular and intermolecular processes for the stoichiometric cleavage of C-H bonds by transition metal complexes. The first involves a four-centre transition state {Figure 1-2}, which is believed to be important for electron-deficient early transition metal, actinide and lanthanide hydride and alkyl complexes in their group oxidation state. This

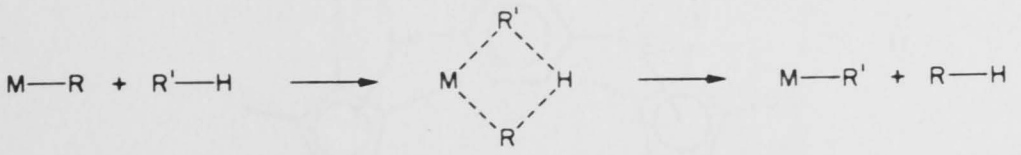


Figure 1-2: Proposed pathway for C-H activation in early transition metal complexes.

pathway was first suggested to explain the deuterium substitution pattern resulting from hydrogenolysis of the zirconium alkyl hydrides $ZrHR(\eta^5\text{-}C_5H_5)_2$ to form alkanes and $[ZrH_2(\eta^5\text{-}C_5H_5)_2]_n$.[68] Extended Hückel M.O. calculations for the hydrogenolysis of $ZrHMe(\eta^5\text{-}C_5H_5)_2$ indicated that the reaction proceeded via co-ordination of dihydrogen, formation of the four-membered transition state, rearrangement to a methane complex and subsequent dissociation of methane {Figure 1-3}. A similar mechanism was determined for H/D exchange of the hydride ligands in $[ZrH_2(\eta^5\text{-}C_5H_5)_2]_n$.[29]

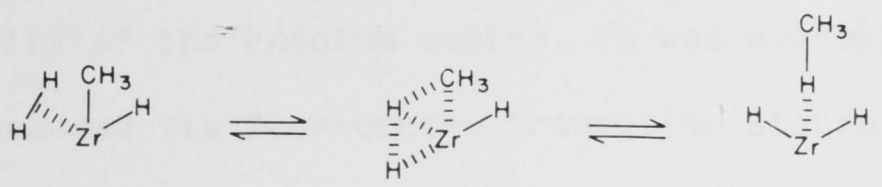
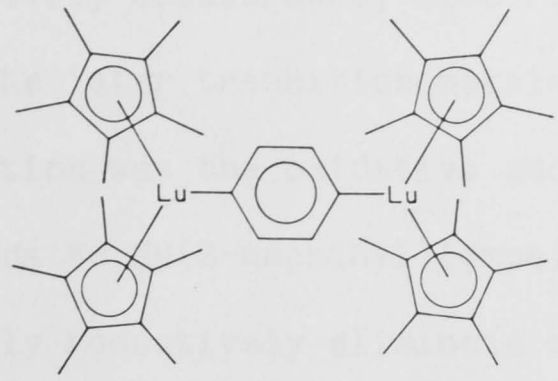


Figure 1-3: Pathway for hydrogenolysis of $ZrHMe(\eta^5\text{-}C_5H_5)_2$.

Subsequently, an analogous pathway was invoked in the reactions of scandium,[167] ytterbium and lutetium[175] alkyls and hydrides with alkane and arene C-H bonds, as well as in the cyclometallation reactions of thorium neopentyl and trimethylsilyl[38]



[11]

and uranium and thorium bis(trimethylsilyl)amide[163] complexes. A wide variety of alkanes has been activated by these electron deficient species, including TMS,[61,176] methane,[61,167,175] and benzene.[38,85,167,175] Benzene has also been dimetallated, forming the lutetium complex [11].[176] H/D exchange was also observed between hydrogen, solvent and ligand sites in a number of these complexes,[85,163,167,176] and this probably proceeds via a similar mechanism.

A number of silica-supported rhodium(III) allyl species catalyse H/D exchange in butane[174] and cleave methane C-H bonds to form both hydride and methylrhodium species.[120] In view of the electrophilicity of the rhodium centre, it was suggested that these reactions proceeded via four-centre transition states.

The second major mechanism for stoichiometric cleavage of alkyl and aryl C-H bonds by transition metal compounds is oxidative addition to a metal centre*. This reaction occurs in complexes

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* A third mechanism, attack by radicals, will not be discussed here. A number of these systems exist, for example, $[Rh(octaethylporphyrin)]_2$;[178] however, the mechanistic details of these reactions are still not clear.

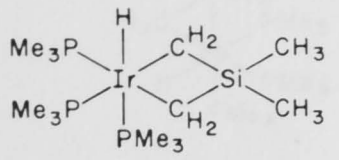
containing co-ordinatively unsaturated, electron-rich metal centres, generally, those of the later transition metals. One of the earliest examples of this reaction was the oxidative addition of sp, sp^2 and activated sp^3 C-H bonds to $MH(2\text{-naphthyl})(dmpe)_2$ {M = Fe, Ru}, compounds which readily reductively eliminate naphthalene to form the reactive intermediate $M(dmpe)_2$.[102,169] Photolysis of the compounds $WH_2(\eta^5\text{-}C_5H_5)_2$, $W(\eta^5\text{-}C_5H_5)_2CO$,[78] $Ir(\eta^5\text{-}C_5H_5)(CO)_2$,[96] $Ir(\eta^5\text{-}C_5Me_5)(CO)_2$,[95,96] $IrH_2(\eta^5\text{-}C_5Me_5)(PMe_3)$,[105] $RhH_2(\eta^5\text{-}C_5Me_5)(PMe_3)$,[111,148] and $RuH_2(\eta^6\text{-arene})(PR_3)$[124] and the thermolysis of $WH(CH_3)(\eta^5\text{-}C_5H_5)_2$[78] and $IrHCy(\eta^5\text{-}C_5Me_5)(PMe_3)$[177] was found to give co-ordinatively unsaturated intermediates which subsequently undergo oxidative addition of alkane and arene C-H bonds. Among these systems, $IrH_2(\eta^5\text{-}C_5Me_5)(PMe_3)$ [12] and $RhH_2(\eta^5\text{-}C_5Me_5)(PMe_3)$ [13] have been studied most intensively, and a great deal of mechanistic information, including relative selectivities of C-H bond scission, has been obtained.

Irradiation of $MH_2(\eta^5\text{-}C_5Me_5)(PMe_3)$ {M = Rh, Ir} is believed to yield initially the co-ordinatively unsaturated species $M(\eta^5\text{-}C_5Me_5)(PMe_3)$. One piece of evidence for this proposition was the isolation of $Rh(\eta^5\text{-}C_5Me_5)(CO)(PMe_3)$ from the irradiation of [13] at low temperature in a solution containing CO.[148] In aromatic solvents, it is thought that an intermediate dihapto-arene complex $M(\eta^5\text{-}C_5Me_5)(\eta^2\text{-arene})(PMe_3)$ may be formed, since $Rh(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}p\text{-}C_6H_4Bu^t_2)(PMe_3)$ was formed by reductive elimination of methylcyclohexane-d_{14} from $RhD(CD_2C_6D_{11})(\eta^5\text{-}C_5Me_5)(PMe_3)$ in the presence of $p\text{-}C_6H_4Bu^t_2$.[111] Corroboration for the oxidative addition pathway as opposed to alternative radical pathways or heterolytic reactions came from photolysis of [12] in a mixture of neopentane and cyclohexane-d_{12}. The predominant products were

$IrH(CH_2CMe_3)(\eta^5\text{-}C_5Me_5)(PMe_3)$ and $IrD(C_6D_{11})(\eta^5\text{-}C_5Me_5)(PMe_3)$. Only a small quantity of the isotopically scrambled complexes was observed. Similarly, photolysis of [12] in cyclopropane formed only the cyclopropyl hydride complex; no product arising from cleavage of the highly strained C-C bonds was observed.[105]

The selectivity of C-H bond scission by these iridium and rhodium systems was studied by determining the product distribution in a variety of reactions. On irradiating [13] in toluene, two isomers of $RhH(C_6H_4CH_3)(\eta^5\text{-}C_5Me_5)(PMe_3)$ were formed in a 2:1 ratio, arising from attack on the meta and para positions of the aromatic ring; indicating that the rhodium centre did not discriminate between these two sites. However, when the irradiation was carried out at low temperature, the ortho and benzyl products were also formed, indicating a relatively small difference in activation energies for oxidative addition at the various positions.[111] Intermolecular selectivities were determined by irradiating [12] or [13] in mixtures of solvents. When the irradiation was carried out at low temperature, kinetic products were observed. In general, the preference for C-H bond attack was aryl > 1° > 2° {not observed for Rh} >> 3° {never observed}, with rhodium being much more selective than iridium.[106] Reductive elimination of alkane occurred readily above -20° for the rhodium complexes,[106,111] but the iridium complexes apparently only underwent reductive elimination at an appreciable rate above 110°.[105,177] For example, the hydridomethyl complex $IrH(CH_3)(\eta^5\text{-}C_5Me_5)(PMe_3)$ was prepared by reductive elimination of cyclohexane from $IrHCy(\eta^5\text{-}C_5Me_5)(PMe_3)$ at 140° in the presence of methane.[177]

Oxidative addition steps are also believed to be involved in the reaction of $MMe_2(\eta^5\text{-}C_5Me_5)(dmso)$ {M = Ir, Rh} with arenes to form



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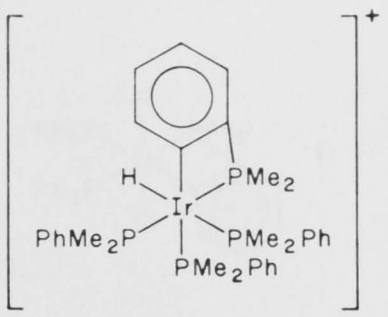
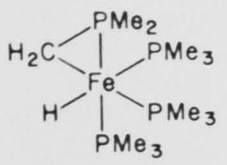


[15]

$MMe_{2-n}Ar_n(\eta^5\text{-}C_5Me_5)(dmso)$ {n = 1, 2}.[76] This reaction was proposed to proceed by dissociation of dmso, oxidative addition of an arene C-H bond to form an iridium(V) or rhodium(V) intermediate, and subsequent reductive elimination of methane. Co-ordination of dmso completed the process. The proposal of iridium(V) and rhodium(V) intermediates is not as unusual as it might at first appear. The stable iridium(V) and rhodium(V) compounds $MR_2R'_2(\eta^5\text{-}C_5Me_5)$ {M = Ir, Rh, R = H, R' = $SiEt_3$; M = Ir, R = R' = Me} have recently been described.[62,63,101]

Intramolecular oxidative addition of C-H bonds to give cyclometallated complexes is a well known process. An example of this is the formation of the iridasilacyclobutane fac-$\overline{IrH(CH_2SiMe_2CH_2)}(PMe_3)_3$ [14] by internal oxidative addition of a γ C-H bond in $Ir(CH_2SiMe_3)(PMe_3)_3$.[170] The most commonly encountered cyclometallations are those of phosphine ligands. When $[IrCl(COD)]_2$ was heated with PMe_2Ph, $[Ir(PMe_2Ph)_4]^+$ was believed to be formed. Prolonged heating induced the oxidative addition of an aryl C-H bond, yielding fac-$[\overline{IrH(o\text{-}C_6H_4PMe_2)}(PMe_2Ph)_3]^+$ [15].[57] The sixteen electron complex $IrCl(PPh_3)_3$, a stable orange solid, rapidly cyclometallated to give $\overline{IrHCl(o\text{-}C_6H_4PPh_2)}(PPh_3)_2$ [16] in refluxing benzene.[20] In some cases, this cyclometallation was readily reversible. For example, the iron complex $Fe(PMe_3)_4$ behaved as this species in its reactions



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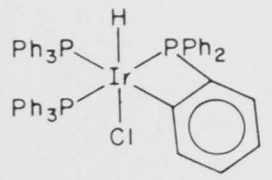
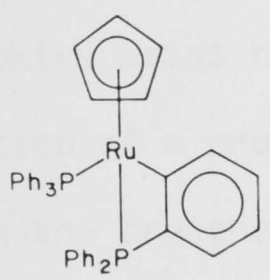


[17]

with CO, and PR_3, and with CO_2 in non-polar solvents, but spectroscopically and in its reactions with acids and with CO_2 in polar solvents it acted as $\overline{FeH(CH_2PMe_2)}(PMe_3)_3$ [17].[87,113,114,115]

Cyclometallation of PPh_3 by thermal elimination of methane from $Ru(CH_3)(\eta^5\text{-}C_5H_5)(PPh_3)_2$ [18] to yield $\overline{Ru(\underline{o}\text{-}C_6H_4PPh_2)}(\eta^5\text{-}C_5H_5)(PPh_3)$ [19][34] presumably proceeds by a C-H bond oxidative addition pathway. The phosphine ligands in $RuX(\eta^5\text{-}C_5H_5)(PPh_3)_2$ are known to be labile,[26] and so the first step is probably dissociation of one of these. Internal oxidative addition of an ortho-phenyl C-H bond in the intermediate $Ru(CH_3)(\eta^5\text{-}C_5H_5)(PPh_3)$ and reductive elimination of methane from the resultant ruthenium(IV) hydridomethyl adduct, and subsequent co-ordination of PPh_3 would give [19]. A similar pathway of C-H oxidative addition and reductive elimination of methane was used to explain the formation of a ruthenium cumulene



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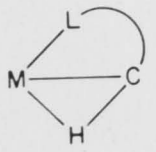
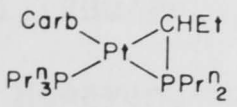


Figure 1-4

complex from [18] and CF_3C_2H.[33] The isolation of stable cyclopentadienylruthenium(IV) complexes such as $[RuXCl(\eta^5\text{-}C_5H_5)(PMe_3)_2]^+$ {X = H, Cl} supports the mechanism described above.[35]

The transition state for internal C-H oxidative additions may be modelled by stable compounds containing "agostic" interactions, in which a C-H bond co-ordinates to an otherwise co-ordinatively unsaturated metal atom {Figure 1-4}.[31] These interactions are essentially three-centre two electron bonds, although they are often in flux with both limiting structures {hydridometallacycle and unsaturated metal alkyl}. The trajectory of C-H bond cleavage by oxidative addition to a metal atom has been modelled using all known structures containing agostic alkyl groups.[52] Ab initio[125,142] and extended Hückel[59] calculations on the model compounds $TiHRCl_2(PH_3)_2$ and $[TiH_5(CH_3)]^{2-}$ show that agostic interactions result in a lower total energy for these models.

Some tertiary phosphine metal halide complexes undergo cyclometallation by abstraction of a proton from an alkyl substituent on the tertiary phosphine in the presence of a strong base. A general feature of these reactions is that the α-carbon atom of an alkyl chain is preferentially metallated. For example, treatment of



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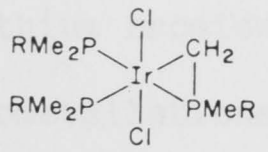
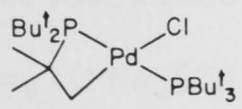


[21] {R = Me, Ph}

<u>trans</u>-$PtCl_2(PPr^n_3)_2$ with lithium 2-phenyl-1,2-dicarba-<u>closo</u>-dodecaborane (LiCarb) gave the complex $\overline{Pt(Carb)(CHEtPPr^n_2}(PPr^n_3)$ [20].[27,28] Similarly, treatment of <u>mer</u>-$IrCl_3(PMe_2R)_3$ with $LiNPr^i_2$, $LiBu^n$ or $Li(CH_2)_5Li$ gave $\overline{IrCl_2(CH_2}PMeR)(PMe_2R)_2$ {R = Me, Ph} [21].[3] It is significant that the site of metallation of dimethylphenylphosphine in this case is different from that in the oxidative addition reaction of $[Ir(PMe_2Ph)_4]^+$ cited above, since the base mediated reaction is dependent on the acidity of the protons α to phosphorus.

There is a formal resemblance between these base assisted cyclometallations and cyclometallations in which HCl is spontaneously lost. Examples of this are the conversion of <u>trans</u>-$PdCl_2(PBu^t_3)_2$ into a 1:1 mixture of $(Bu^t_3PH)_2(PdCl_4)$ and $\overline{PdCl(CH_2CMe_2}PBu^t_2)(PBu^t_3)$ [22],[75] the reaction of <u>trans</u>-$PtCl_2(PPh\underline{o}\text{-}Tol_2)_2$ to give



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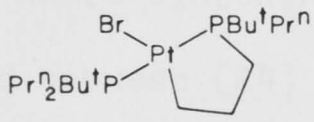

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$\overline{PtCl(\underline{o}\text{-}CH_2C_6H_4PPh\underline{o}\text{-}Tol)}(PPh\underline{o}\text{-}Tol_2)$ and the formation of a mixture of trans-$PtBr_2(PBu^tPr^n_2)_2$ and $\overline{PtBr(CH_2CH_2CH_2PBu^tPr^n)}(PBu^tPr^n_2)$ [23] on heating trans-$PtCl_2(PBu^tPr^n_2)_2$ with lithium bromide in 2-methoxyethanol.[46] However, these cyclometallations probably proceed by oxidative addition of a C-H bond to the metal {$PBu^tPr^n_2$ was metallated at the terminal rather than the α carbon atom}. Reductive elimination of HCl from the metal(IV) intermediates would give the observed products; reductive elimination of HCl from platinum(IV) chlorohydrides has been known for a long time.[45]

Whilst the selectivity of external C-H bond activation in oxidative addition reactions has been studied to some extent for $M(\eta^5\text{-}C_5Me_5)L$ {M = Rh, Ir, L = PMe_3, CO}, the selectivity of competing intramolecular and intermolecular C-H bond scission, and the factors controlling this selectivity, have not been established. Photolysis of $IrH_2(\eta^5\text{-}C_5Me_5)(PPh_3)$ in benzene formed two products, one due to cyclometallation, the other due to solvent C-H bond scission, whereas when the trimethylphosphine analogue was photolyzed in benzene, external C-H bond attack was the sole outcome.[105] Similarly, photolysis of $RhH_2(\eta^5\text{-}C_5Me_5)(PMe_3)$ in hydrocarbon solvents gave products arising exclusively from external C-H bond cleavage,[111] whereas photolysis of $RhH_2(\eta^5\text{-}C_5Me_5)(PMe_2Pr^n)$ in n-propane gave $RhH(C_3H_7)(\eta^5\text{-}C_5Me_5)(PMe_2Pr^n)$ as the kinetic product, but $\overline{RhH(CH_2CH_2CH_2PMe_2)}(\eta^5\text{-}C_5Me_5)$ [24] as the thermodynamic product.[112] An equilibrium was established between $\overline{RhH(\underline{o}\text{-}C_6H_4CH_2PMe_2)}(\eta^5\text{-}C_5Me_5)$ and $RhH(C_6H_5)(\eta^5\text{-}C_5Me_5)(PMe_2[CH_2Ph])$ and between [24] and $RhH(C_6H_5)(\eta^5\text{-}C_5Me_5)(PMe_2Pr^n)$ in benzene, with the equilibrium lying heavily towards the cyclometallated compounds.[112]

The factors determining the selectivity of intramolecular as opposed to intermolecular C-H bond activation clearly require elucidation. This possibly can be done by varying the phosphine ligand. The choice of the areneruthenium system as being suitable for these studies is based on the ready availability of a wide variety of areneruthenium precursor complexes $[RuCl_2(\eta^6\text{-arene})]_2$, the facile synthesis of a wide variety of phosphine complexes in this system, and on the promising initial results already mentioned in this Introduction. Phosphine complexes are also suitable because phosphorus chemical shifts are a very sensitive probe for the formation of four or five-membered rings,[67] and thus $^{31}P[^1H]$ NMR spectroscopy is a powerful diagnostic tool for the detection of cyclometallated products. The range of phosphine ligands available is enormous, and this possibly offers an unprecedented opportunity to also determine the selectivity of cyclometallation reactions.

The aim of this thesis, therefore, is to determine the selectivity of the unsaturated ruthenium(0) fragment $Ru(\eta^6\text{-arene})(PR_3)$ in its reactions with internal and external C-H bonds, and to elucidate the factors which control these reactions.

CHAPTER 2

THE SYNTHESIS OF DICHLORO AND CHLOROHYDRIDO COMPLEXES

The chloro complexes $RuCl_2(PPh_3)_3$,[86,151] $RuCl_2(dmpe)_2$,[44,168] trans-$RuCl_2(PMe_3)_4$,[166,183] $RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2$[26] and $RuCl_2(\eta^6\text{-arene})(PR_3)$[24,97,180] and the hydrido complexes $RuHCl(PPh_3)_3$[50] and $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$[14,97] have proven to be useful precursors for the synthesis of a wide range of organoruthenium complexes. This chapter is concerned with the synthesis and characterization of $RuCl_2(\eta^6\text{-arene})(PR_3)$ and $RuHCl(\eta^6\text{-}C_6Me_6)L$ which are the precursors of the cyclometallated and hydridoaryl complexes described in Chapter 3.

The synthesis of a number of tertiary phosphine complexes $RuCl_2(\eta^6\text{-arene})(PR_3)$ has been reported;[24,100,152,180,184,186,190] however, only recently have complexes of this type containing sterically demanding phosphines been made.[138,181] Such complexes are of interest because the presence of bulky ligands, generally, those more sterically demanding than PPh_3, is known to stabilize hydrido complexes such as trans-$PtH_2(PR_3)_2$[128,161,187] and trans-$PtHR'(PR_3)_2$ {R' = methyl, phenyl},[1,5] and to promote cyclometallation.[46]

Few syntheses of the hydridoruthenium complexes $RuHCl(\eta^6\text{-}C_6Me_6)(PR_3)$ have been reported.[16,165] Heating of $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ with two equivalents of PPh_3 and excess sodium carbonate in aqueous 2-propanol was reported to give $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ in 59% yield.[165] The mesitylene analogue was similarly prepared. Later, it was reported that $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ could be made in 98% yield by heating $RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_3)$ with sodium carbonate in 2-propanol,[16] but subsequent attempts in this laboratory to repeat the latter synthesis invariably resulted in yields of 35% or less. A recent communication

briefly mentioned the synthesis of the hydrides $RuHX(\eta^6\text{-}C_6R_6)(PR'_3)$ {X = Cl, O_2CCF_3} by reaction of $RuX_2(\eta^6\text{-}C_6R_6)(PR'_3)$ with zinc dust in methanol.[182]

RESULTS AND DISCUSSION

1) DICHLORO COMPLEXES

Treatment of $[RuCl_2(\eta^6\text{-arene})]_2$ {arene = benzene, mesitylene} with an excess of the tertiary phosphines L {L = PBu^tPh_2, PPr^i_3, PCy_3} split the chloro bridges, forming the complexes $RuCl_2(\eta^6\text{-arene})L$ in poor to moderate yield {see Figure 2-1}. Unlike earlier preparations of $RuCl_2(\eta^6\text{-arene})L$ {L = P(n-alkyl)$_3$, P(aryl)$_3$, P(OR)$_3$},[24,97] there was no evidence of arene displacement. During the course of this work, the synthesis of $RuCl_2(\eta^6\text{-}C_6H_6)(PPr^i_3)$ was independently described.[181] These compounds are red or orange air-stable solids which are air-sensitive in solution. The infrared spectra of these species show two bands due to ν(RuCl) in the region 260-300cm^{-1} as expected for a "piano-stool" type of structure. The peaks due to ν(RuCl) were the most intense peaks observed in the far infrared spectra of all the dichloro complexes studied. The $^{31}P[^1H]$ NMR spectra of these compounds, with the exception of

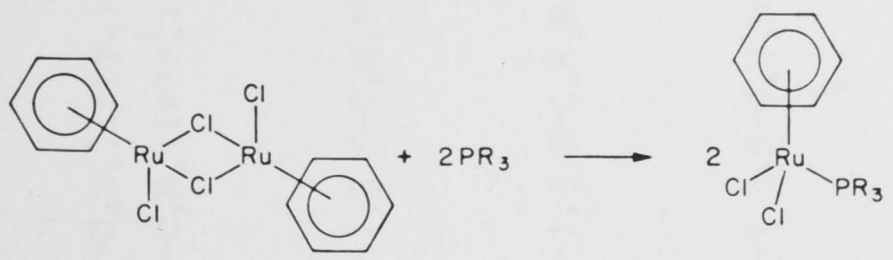


Figure 2-1: Formation of Dichloro Complexes.

Table 2-1: ^{1}H and ^{31}P NMR Data for Dichloro Complexes[a]

Compound	δ(P)	δ(arene)	Other
$RuCl_2(\eta^6\text{-}C_6H_6)(PBu^tPh_2)$	31.3	5.28	1.34 (d, $^3J_{PH}$=16, $C\underline{Me}_3$); 7.3-7.6, 7.8-8.2 (m, $C_6\underline{H}_5$)
$RuCl_2(\eta^6\text{-}C_6H_6)(PCy_3)$	30.2	5.70	1.0-2.7 (m, $C_6\underline{H}_{11}$)
$RuCl_2(\eta^6\text{-}C_6H_6)(PPr^i_3)$	40.4	5.72	1.34 (dd, $^3J_{HH}$=7, $^3J_{PH}$=13, $CH\underline{Me}_2$); 2.6-3.1 (br m, $PC\underline{H}Me_2$)
$RuCl_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PBu^tPh_2)$	25.7	4.53($C_6\underline{H}_3Me_3$) 1.74($C_6H_3\underline{Me}_3$)	1.19 (d, $^3J_{PH}$=14, $C\underline{Me}_3$); 7.3-7.5,8.1-8.3 (m, $C_6\underline{H}_5$)
$RuCl_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PCy_3)$[b]	27.5	5.03($C_6\underline{H}_3Me_3$) 2.17($C_6H_3\underline{Me}_3$)	1.1-2.7 (m, $C_6\underline{H}_{11}$)
$RuCl_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PPr^i_3)$	38.5[c,d] 33.6	5.03($C_6\underline{H}_3Me_3$) 2.20($C_6H_3\underline{Me}_3$)	1.35 (dd, $^3J_{HH}$=8, $^3J_{PH}$=14, $CH\underline{Me}_2$)
$RuCl_2(\eta^6\text{-}1,2,4,5\text{-}C_6H_2Me_4)(PPh_3)$	26.6	4.50($C_6\underline{H}_2Me_4$) 1.86($C_6H_2\underline{Me}_4$)	7.2-8.0 (m, $C_6\underline{H}_5$)

Table 2-1: ^{1}H and ^{31}P NMR Data for Dichloro Complexes (Cont'd)

Compound	δ(P)	δ(arene)	Other
$RuCl_2(\eta^6\text{-}C_6Me_6)(PPr^i_3)$	37.0[d] 28.6 20.7	2.00	1.1-1.5 (m, $CH\underline{Me}_2$); 2.3-2.9 (m, $C\underline{H}Me_2$)
$RuCl_2(\eta^6\text{-}C_6Me_6)(PBu^tPh_2)$	24.0(br)[d] 17.9(br)	1.99[d] 1.53	1.04 (d, $^3J_{PH}$=13, $C\underline{Me}_3$); 7.3-7.5, 8.1-8.4(m, $C_6\underline{H}_5$)
$RuCl_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$	25.1	2.06	1.19 (d, $^3J_{PH}$=13.2, $C\underline{Me}_3$); 1.38 (d, $^2J_{PH}$=9.8, $P\underline{Me}$)
$RuCl_2(\eta^6\text{-}C_6Me_6)(PEtPh_2)$	28.5	1.71	0.72 (dt, $^3J_{PH}$=15.4, $^3J_{HH}$=7.6, $CH_2C\underline{H}_3$); 2.59 (dq, $^2J_{PH}=^3J_{HH}$=7.6, $C\underline{H}_2CH_3$); 7.2-7.5, 7.8-8.0 (m, $C_6\underline{H}_5$)
$RuCl_2(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$	8.9	1.79	1.72 (d, $^2J_{PH}$=10.7, $P\underline{Me}$); 7.3-7.5,7.7-7.9 (m, $C_6\underline{H}_5$)
$RuCl_2(\eta^6\text{-}C_6Me_6)(P[OMe]_3)$	120.4	2.04	3.76 (d, $^3J_{PH}$=10.7, $O\underline{Me}$)
$RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_2\underline{o}\text{-Tol})$	31.8[d] -12.8	1.77[d] 1.56	1.96, 2.02 ($\underline{o}\text{-}C\underline{H}_3C_6H_4$)[d]; 7-8 (m, $C_6\underline{H}_4$, $C_6\underline{H}_5$).

a: In $CDCl_3$ at ambient temperature, δ in ppm, J in Hz.
b: Characterized by NMR and IR spectroscopy only.
c: Peak intensity 38:1 (δ 38.5 : δ 33.6).
d: For explanation see text.

Table 2-2: Infrared Data for Dichloro Complexes[a]

Compound	ν(Ru-Cl) (cm^{-1})
$RuCl_2(\eta^6\text{-}C_6H_6)(PBu^tPh_2)$	272, 289
$RuCl_2(\eta^6\text{-}C_6H_6)(PCy_3)$	270, 290
$RuCl_2(\eta^6\text{-}C_6H_6)(PPr^i_3)$	261, 283
$RuCl_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PBu^tPh_2)$	274, 296
$RuCl_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PCy_3)$[b]	275, 290
$RuCl_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PPr^i_3)$	270, 298
$RuCl_2(\eta^6\text{-}1,2,4,5\text{-}C_6H_2Me_4)(PPh_3)$	288, 300
$RuCl_2(\eta^6\text{-}C_6Me_6)(PPr^i_3)$	282(br sh), 296
$RuCl_2(\eta^6\text{-}C_6Me_6)(PBu^tPh_2)$	280(br sh), 291(br)
$RuCl_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$	296(br)
$RuCl_2(\eta^6\text{-}C_6Me_6)(PEtPh_2)$	(276, 289, 303)
$RuCl_2(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$	290(br sh),302
$RuCl_2(\eta^6\text{-}C_6Me_6)(P[OMe]_3)$	290, (316 ?)

a: Polythene disc; br = broad, sh = shoulder. These peaks were the strongest bands in the far infrared spectra.
b: Characterized by NMR and IR spectroscopy only.

$RuCl_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PPr^i_3)$, displayed only one resonance. The characterization of $RuCl_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PCy_3)$ is incomplete because of the very low yield of this compound (6%). There was no reaction between $[RuCl_2(\eta^6\text{-arene})]_2$ and PBu^t_2Ph.

The $^{31}P[^1H]$ NMR spectrum of $RuCl_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PPr^i_3)$ showed two resonances, one at δ 38.5ppm, the other, of much lower intensity, at 33.6ppm. This observation was not investigated further, but this phenomenon is probably due to rotamers. Rotamers arising from restricted rotation about the Pd-P bonds were observed by ^1H NMR spectroscopy in solutions of the palladium complex $PdCl_2(PBu^t_2\underline{o}\text{-Tol})_2$.[48] In the case of $RuCl_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PPr^i_3)$, there probably was restricted rotation about the P-C bonds, the rotamers arising from different arrangements of the isopropyl groups about phosphorus. Similar behaviour was observed for $RuCl_2(\eta^6\text{-}C_6Me_6)(PPr^i_3)$ and $RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_2\underline{o}\text{-Tol})$ {see below}.

Treatment of $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ with an excess of PBu^tPh_2 or PPr^i_3 gave the complexes $RuCl_2(\eta^6\text{-}C_6Me_6)(PR_3)$ as orange air-stable solids, which were air-sensitive in solution. However, there was no reaction between $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ and the ligands PCy_3, PBu^t_2Ph or $PBu^t_2Pr^n$. This was presumably because the adducts $RuCl_2(\eta^6\text{-}C_6Me_6)L$ formed by these ligands would be sterically very hindered. This hypothesis was supported by the spectroscopic behaviour of $RuCl_2(\eta^6\text{-}C_6Me_6)(PBu^tPh_2)$ and $RuCl_2(\eta^6\text{-}C_6Me_6)(PPr^i_3)$.

The $^{31}P[^1H]$ NMR spectrum of $RuCl_2(\eta^6\text{-}C_6Me_6)(PBu^tPh_2)$ showed two broad resonances at δ 24.0 and 17.9ppm, the latter being due to free phosphine {cf. lit. δ 17.3ppm[135]}. The ^1H NMR spectrum of $RuCl_2(\eta^6\text{-}C_6Me_6)(PBu^tPh_2)$ also displayed a resonance at δ 1.99ppm due

to $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$. Phosphine dissociation occurred both in CD_2Cl_2 and in $CDCl_3$. The $^{31}P[^1H]$ NMR spectrum of $RuCl_2(\eta^6\text{-}C_6Me_6)(PPr^i_3)$ was more complex, exhibiting resonances at δ 37.0, 28.6 and 20.7ppm in the approximate ratio 2:2:1. The resonance at δ 20.7ppm was due to free PPr^i_3 {cf. lit. δ 19.4ppm[83]}. Addition of PPr^i_3 to the solution resulted in only a slight increase in intensity of the resonance at δ 28.6ppm relative to that at δ 37.0ppm. This behaviour was not investigated further, but like $RuCl_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PPr^i_3)$, the peaks at δ 37.0 and 28.6ppm were probably due to rotamers of $RuCl_2(\eta^6\text{-}C_6Me_6)(PPr^i_3)$. The air-sensitivity of these complexes in solution, and that of their benzene and mesitylene analogues, was presumably due to the oxidation of the dissociated phosphine.

The complex $RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_2\underline{o}\text{-Tol})$ [25] has been described previously,[97] but its characterization was not adequate. In particular, its $^{31}P[^1H]$ NMR spectrum in CD_2Cl_2 was described as consisting of a singlet at δ -56.4ppm,[97] which is clearly untenable, since no simple tertiary phosphine complex of ruthenium(II) is known to have a phosphorus resonance at such high field.

Complex [25] was synthesized by treating $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ with a slight excess of $PPh_2\underline{o}$-Tol. It was found to be a pink, poorly soluble, light, feathery solid which slowly lost occluded chloroform. This made a satisfactory elemental analysis difficult to obtain, especially because carbon/hydrogen and chlorine analyses were made one week apart. The ^1H NMR spectrum of [25] in $CDCl_3$ showed singlets at δ 1.77 and 1.56ppm in the ratio 2.8:1 due to co-ordinated hexamethylbenzene, and at δ 2.02 and 1.96ppm in the ratio 1:2.8 due to the ortho-methyl protons. The $^{31}P[^1H]$ NMR spectrum of [25] in $CDCl_3$ consisted of two singlets at δ 31.8 and -12.8ppm in the ratio of

approximately 15:1; neither of these is due to free PPh_2o-Tol which has its ^{31}P resonance at δ 22.5ppm in $CDCl_3$. The resonance at δ 31.8ppm was due to [25]. The nature of the species giving rise to the resonance at δ -12.8ppm is not known. The two sets of resonances in the ^1H NMR spectra are probably due to rotamers arising from restricted rotation about the ortho-tolyl C-P bond, but it is not clear why they are not evident in the $^{31}P[^1H]$ NMR spectrum.

Treatment of $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ with a slight excess of the ligands PBu^tMe_2, $PEtPh_2$, PMe_2Ph and $P[OMe]_3$ generated the red complexes $RuCl_2(\eta^6\text{-}C_6Me_6)(PR_3)$, which were air stable as solids and in solution. The adducts showed single resonances in their $^{31}P[^1H]$ NMR spectra.

Although these complexes undoubtedly have the usual "piano-stool" structure, it was not straightforward to assign ν(RuCl) in the infrared spectra of these species {see Table 2-2}. The infrared spectrum of $RuCl_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ shows a single broad band at 296cm^{-1}, whilst that of $RuCl_2(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$ exhibited a peak at 302cm^{-1} with a shoulder at 290cm^{-1}. The $PEtPh_2$ analogue showed three equally intense bands at 276, 289 and 302cm^{-1}. It is possible that only two of these peaks are due to ν(RuCl), or that this pattern may be the result of solid state splitting effects. The infrared spectrum of $RuCl_2(\eta^6\text{-}C_6Me_6)(P[OMe]_3)$ displayed a series of low intensity peaks at 230, 258, 290 and 316cm^{-1}. These spectra might have been assigned if the spectra of the bromo analogues $RuBr_2(\eta^6\text{-}C_6Me_6)L$ had been obtained, but no bromo compounds were made.

An interesting feature of the far infrared spectra of both the dichloro complexes which contain methyl-substituted arenes, and of

the chlorohydrido complexes discussed below, was a strong, broad band in the region 220 to 260cm^{-1}. As this peak was absent in the infrared spectra of the benzene complexes $RuCl_2(\eta^6\text{-}C_6H_6)(PR_3)$, it was probably due to an arene-methyl deformation.

The durene complex $RuCl_2(\eta^6\text{-}1,2,4,5\text{-}C_6H_2Me_4)(PPh_3)$ was prepared by treating $[RuCl_2(\eta^6\text{-}1,2,4,5\text{-}C_6H_2Me_4)]_2$ with a slight excess of PPh_3. The $^{31}P[^1H]$ NMR spectrum of this compound showed only one resonance at δ 26.6ppm, and the infrared spectrum displayed the typical two ν(RuCl) bands at 288 and 300cm^{-1}.

2) CHLOROHYDRIDO COMPLEXES

In contrast to the report of Tai-Nang Huang,[97] treatment of $RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_3)$ with EtMgBr did not give the cyclometallated product, $RuH(\underline{o}\text{-}C_6H_4PPh_2)(\eta^6\text{-}C_6Me_6)$ [27]. However, treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ with methyllithium afforded [27]. As a consequence, chlorohydrido complexes with a wide range of phosphorus donor ligands were prepared as precursors for the cyclometallated and hydridoaryl complexes reported in Chapter 3.

Although the preparation of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ had been reported, no general method for synthesizing a range of complexes of this type could be found. After considerable effort, four useful procedures were developed:

Method A : Heat a suspension of $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ with an excess of the ligand and sodium carbonate in refluxing anhydrous 2-propanol for 15h.

Method B : Heat a suspension of $RuCl_2(\eta^6\text{-}C_6Me_6)L$ with an excess of sodium carbonate in refluxing anhydrous 2-propanol for 15h.

Method C : Heat $RuHCl(\eta^6\text{-}C_6Me_6)(AsPh_3)$ with an excess of ligand in toluene at 70° for 16h.

Method D : Heat $RuHCl(\eta^6\text{-}C_6Me_6)(SbPh_3)$ with an excess of ligand in toluene at 70° for 16h.

The general work-up procedure for these compounds was to evaporate the reaction mixture to dryness, extract with toluene and crystallize the hydride by the addition of n-hexane. In some instances, this procedure was modified. A summary of these syntheses is presented in Table 2-3. Before describing these in detail, the characterization of the chlorohydrides will be discussed.

Spectroscopic Properties

The hydrido complexes $RuHCl(\eta^6\text{-}C_6Me_6)L$ were yellow to orange microcrystalline or crystalline solids. They were air-sensitive, but were readily handled in the air as solids for short periods. In solution, they decomposed on exposure to air over about an hour, the solutions turning black and often forming a black precipitate. The infrared spectra showed a broad, medium intensity band in the region 1880-2030cm^{-1} due to ν(RuH) {peak width at half-height usually 20-40cm^{-1}}, the complexes with bulky ligands generally having ν(RuH) at higher energy. There was also a single peak in the far infrared region due to ν(RuCl), in the range 280-305cm^{-1} {see Table 2-6}. The far infrared spectra also had a strong, broad band between 220 to 260cm^{-1} which was also in the infrared spectra of the dichloro derivatives with methyl substituted arenes. As noted earlier, this band was probably due to an arene-methyl deformation mode.

Table 2-3 : Summary of Syntheses of $RuHCl(\eta^6\text{-}C_6Me_6)L$

Method A: $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ + L + Na_2CO_3 in refluxing 2-propanol/15h

B: $RuCl_2(\eta^6\text{-}C_6Me_6)L$ + Na_2CO_3 in refluxing 2-propanol/15h

C: $RuHCl(\eta^6\text{-}C_6Me_6)(AsPh_3)$ + L in toluene at 70°/16h

D: $RuHCl(\eta^6\text{-}C_6Me_6)(SbPh_3)$ + L in toluene at 70°/16h

L	Method	Mole Ratio L:Ru	Yield (%)	Remarks
PPh_3	A	2.5:1	65	
	B		35	
$AsPh_3$	A	2:1	80	Heat 3h, recrystallize from CH_2Cl_2/Et_2O.
$SbPh_3$	A	1.5:1	75	Heat 3h, recrystallize from THF/n-hexane.
$P[OPh]_3$	D	1.2:1	51	
$P[\underline{p}\text{-}C_6H_4F]_3$	A	2.5:1	68	
$P[\underline{p}\text{-}C_6H_4CH_3]_3$	A	1.06:1	46	
$P[\underline{p}\text{-}C_6H_4OCH_3]_3$	A	2:1	0	
	B		21	Heat 60h, filter toluene extract through filter aid.
	D	2:1	40	
$PPh_2(\underline{o}\text{-Tol})$	B		0	Forms $\overline{RuCl(\underline{o}\text{-}CH_2C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$ [26].
	D	1.3:1	66	Filter toluene extract through filter aid.
PBu^tPh_2	A	3:1	60	
	B		50	
PPh_2Pr^n	C	2:1	80	
PPh_2Pr^i	A	5:1	65	

Table 2-3 : Summary of Syntheses of $RuHCl(\eta^6\text{-}C_6Me_6)L$ (Cont'd)

L	Method	Ratio L:Ru(atoms)	Yield (%)	Remarks
$PEtPh_2$	C	1.5:1	65	
$PMePh_2$	C	2.5:1	78	
PMe_2Ph	B		43	Heat 38h, evaporate to dryness, extract with CH_2Cl_2; elute from alumina with CH_2Cl_2.
PMe_3	B		75	
$P[OMe]_3$	D	1.5:1	32	
PEt_3	D	1.6:1	57	
PPr^i_3	A	3:1	58	
PCy_3	A	2:1	57	
PBu^tMe_2	B		74	
PBu^t_2Me	A	3.5:1	64	
PBu^t_2Et	A	4:1	43	
$PBu^t_2Pr^n$	A	2.3:1	21	Heat 3h, load toluene extract onto alumina column, elute with hexane and discard eluate. Elute with CH_2Cl_2.

Table 2-4: ^{1}H and ^{31}P NMR Data for Hydrido Complexes[a]

Compound	δ(P)	δ($C_6\underline{Me}_6$)	δ(Ru$\underline{H}$) ($^{2}J_{PH}$)	Other
RuHCl(η⁶-C_6Me_6)($AsPh_3$)		1.78	-7.32	6.9-7.1, 7.8-7.9 (m, $C_6\underline{H}_5$)
RuHCl(η⁶-C_6Me_6)($SbPh_3$)		1.89	-7.16	7.0-7.2, 7.8-7.9 (m, $C_6\underline{H}_5$)
RuHCl(η⁶-C_6Me_6)(P[OPh]$_3$)	135.7	1.71	-9.34(58.1)	6.7-6.9, 7.0-7.1, 7.5-7.6 (m, $C_6\underline{H}_5$)
RuHCl(η⁶-C_6Me_6)(P[$\underline{p}$-C_6H_4F]$_3$)	55.9	1.62	-8.56(54.7)	6.6-6.8, 7.5-7.7, (m, $C_6\underline{H}_4$)[b]
RuHCl(η⁶-C_6Me_6)(P[$\underline{p}$-$C_6H_4CH_3$]$_3$)	55.9	1.76	-8.21(55.9)	2.00 (s, $C_6H_4C\underline{H}_3$); 6.9-7.0, 7.8-8.0 (m, $C_6\underline{H}_4$)
RuHCl(η⁶-C_6Me_6)(P[$\underline{p}$-$C_6H_4OCH_3$]$_3$)	52.5	1.79	-8.21(54.7)	3.22 (s, $OC\underline{H}_3$); 6.7-6.8, 7.8-8.0 (m, $C_6\underline{H}_4$)
RuHCl(η⁶-C_6Me_6)($PPh_2\underline{o}$-Tol)	52.9	1.71	-8.13(54.7)	2.21 (s, $C_6H_4C\underline{H}_3$); 6.8-7.3, 7.9-8.3 (m, $C_6\underline{H}_4$ and $C_6\underline{H}_5$)
RuHCl(η⁶-C_6Me_6)(PBu^tPh_2)	69.8	1.58	-8.54(56)	1.25 (d, $^{3}J_{PH}$ =14, $C\underline{Me}_3$); 6.9-8.5 (m, $C_6\underline{H}_5$)

Table 2-4: ^{1}H and ^{31}P NMR Data for Hydrido Complexes (Cont'd)

Compound	δ(P)	δ($C_6\underline{Me}_6$)	δ(Ru$\underline{H}$) ($^{2}J_{PH}$)	Other
$RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2Pr^n)$	50.7	1.70	-8.67(53.7)	0.76 (apparent t, $^{3}J_{HH}$ = 7, $CH_2CH_2C\underline{H}_3$); One proton multiplets at 1.1[c], 1.5, 1.9[c], 2.8[c] ($C\underline{H}_2C\underline{H}_2CH_3$); 7.0-7.2, 7.7-7.9 (m, $C_6\underline{H}_5$)
$RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2Pr^i)$	64.4	1.64	-8.49(49.8)	0.80 (dd, $^{3}J_{PH}$ = 14.9, $^{3}J_{HH}$ = 7), 1.10 (dd, $^{3}J_{PH}$ = 18.6, $^{3}J_{HH}$ = 8.8) ($CH\underline{Me}_2$); 3.65 (m, $C\underline{H}Me_2$); 7.0-7.3, 7.8-8.1 (m, $C_6\underline{H}_5$)
$RuHCl(\eta^6\text{-}C_6Me_6)(PEtPh_2)$	55.6	1.69	-8.68(53.7)	0.91 (apparent dt, $^{3}J_{PH}$ = 17.6, $^{3}J_{HH}a$ = $^{3}J_{HH}b$ = 7.3, $CH_aH_bC\underline{H}_3$); 1.96 (m, $^{2}J_{H_aH_b}$ = 13.5, $^{2}J_{PH}a$ = 10.8), 2.76 (m, $^{2}J_{PH}b$ = 8.9) ($C\underline{H}_2CH_3$); 7-8 (m, $C_6\underline{H}_5$)
$RuHCl(\eta^6\text{-}C_6Me_6)(PMePh_2)$	39.9	1.72	-8.81(58.1)	1.92 (d, $^{2}J_{PH}$ = 9.8, P$\underline{Me}$); 7-8 (m, $C_6\underline{H}_5$)
$RuHCl(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$	20.2	1.73	-9.24(60.1)	1.39 (d, $^{2}J_{PH}$ = 9.3), 1.68 (d, $^{2}J_{PH}$ = 10.3) (P$\underline{Me}$); 7.0- 7.2, 7.5-7.7 (m, $C_6\underline{H}_5$)
$RuHCl(\eta^6\text{-}C_6Me_6)(PMe_3)$	7.0	1.89	-9.44(62.0)	1.21 (d, $^{2}J_{PH}$ = 9.7, P$\underline{Me}$)

Table 2-4: ^{1}H and ^{31}P NMR Data for Hydrido Complexes (Cont'd)

Compound	δ(P)	$\delta(C_6\underline{Me}_6)$	$\delta(Ru\underline{H})$ ($^{2}J_{PH}$)	Other
$RuHCl(\eta^6\text{-}C_6Me_6)(P[OMe]_3)$	153.5	1.93	-9.50(56.6)	3.66 (d, $^{3}J_{PH}$ = 11.7, O$\underline{Me}$)
$RuHCl(\eta^6\text{-}C_6Me_6)(PEt_3)$	43.31	1.86	-9.30(55.7)	0.96 (dt, $^{3}J_{PH}$ = 15.1, $^{3}J_{HH}a$ = $^{3}J_{HH}b$ = 7.3, $CH_2C\underline{H}_3$); 1.50 (apparent dqu, $C\underline{H}_2CH_3$)
$RuHCl(\eta^6\text{-}C_6Me_6)(PPr^i_3)$	68.9	1.89	-9.13(52)	1.17, 1.20 (overlapping dd, $^{3}J_{HH}$ = 7, $^{3}J_{PH}$ =12, $CH\underline{Me}_2$); 2.05-2.55 (m, $C\underline{H}Me_2$)
$RuHCl(\eta^6\text{-}C_6Me_6)(PCy_3)$	58.9	1.94	-9.18(55)	1.0-2.3 (br m, $C_6\underline{H}_{11}$)
$RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$	33.1	1.88	-9.62(57.6)	1.01 (d, $^{2}J_{PH}$ = 9.8), 1.34 (d, $^{2}J_{PH}$ = 8.8) (P$\underline{Me}$); 1.06 (d, $^{3}J_{PH}$ = 13.2, C$\underline{Me}_3$)
$RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Me)$	55.6	1.84	-8.66(52.2)	0.88 (d, $^{2}J_{PH}$ = 7.3, P$\underline{Me}$); 1.24 (d, $^{3}J_{PH}$ = 12.2), 1.38 (d, $^{3}J_{PH}$ = 12.7) (C$\underline{Me}_3$)
$RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$	80.2	1.89	-9.14(54.8)	1.11 (d, $^{3}J_{PH}$ =11.7), 1.35(d, $^{3}J_{PH}$ = 11.7) (C$\underline{Me}_3$); 1.24 (apparent q, $CH_2C\underline{H}_3$); 1.98-2.3 (br m, $C\underline{H}_2CH_3$)

Table 2-4: ^{1}H and ^{31}P NMR Data for Hydrido Complexes (Cont'd)

Compound	δ(P)	$\delta(C_6\underline{Me}_6)$	$\delta(Ru\underline{H})$ ($^{2}J_{PH}$)	Other
$RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Pr^n)$	77.5	1.89	-9.14(55.2)	1.00 (complex m, $CH_2CH_2C\underline{H}_3$); 1.13 (d, $^{3}J_{PH}$ =11.7), 1.36 (d, $^{3}J_{PH}$ =11.7) ($C\underline{Me}_3$); 1-1.5, 2-2.3 (complex m, $C\underline{H}_2C\underline{H}_2CH_3$)
$RuH_2(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$	24.3	2.04	-10.77(47.6)	1.47 (d, $^{2}J_{PH}$ = 9.2, P$\underline{Me}$); 7.0-7.3, 7.5-7.7 (m, $C_6\underline{H}_5$)
$RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$	42.5	2.17	-11.38(46.4)	1.00 (d, $^{3}J_{PH}$ = 12.8, $C\underline{Me}_3$); 1.13 (d,$^{2}J_{PH}$ = 7.9, P$\underline{Me}$)
$RuH_2(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$	97.4	2.17	-12.52(45.8)	1.13 (d, $^{3}J_{PH}$ = 11.0, $C\underline{Me}_3$); A_3B_2 spin system: 1.3 ($^{3}J_{PH}$ ≈ 14, $CH_2C\underline{H}_3$), 1.5 ($^{2}J_{PH}$ ≈ 8, $C\underline{H}_2CH_3$)

a: In C_6D_6, δ in ppm, J in Hz.

b: δ(F) = -116.1

c: ^{31}P coupled.

Table 2-5: ^{13}C NMR Data For Hydrido Complexes[a]

Compound	δ ($\underline{C}_6Me_6$)	δ($C_6\underline{Me}_6$)	Other
$RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$	96.3(3)	17.2	12.1 ($CH_2\underline{C}H_3$); 17.1 (25, $\underline{C}H_2CH_3$); 30.8, 30.9 ($C\underline{Me}_3$); 36.2 (13), 37.8 (12) ($\underline{C}Me_3$)
$RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Pr^n)$	96.3(0)	17.2	16.8 (12, $CH_2CH_2\underline{C}H_3$); 20.8 ($CH_2\underline{C}H_2CH_3$); 26.8 (24, $\underline{C}H_2CH_2CH_3$); 30.9, 31.0 ($C\underline{Me}_3$); 36.1 (15),37.8 (12) ($\underline{C}Me_3$)
$RuH_2(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$	95.7(3)	18.0	24.9 (32, P$\underline{Me}$)
$RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$	95.2(3)	18.5	19.1 (22, P$\underline{Me}$); 26.6 (6, $C\underline{Me}_3$); 30.9 (28, $\underline{C}Me_3$)
$RuH_2(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$	95.0(3)	18.5	13.0 ($CH_2\underline{C}H_3$); 22.7 (31, $\underline{C}H_2CH_3$); 30.3 (6, $C\underline{Me}_3$); 35.8 (10, CMe_3)

a: In C_6D_6, δ in ppm, J_{PC} (in parentheses) in Hz. Aromatic carbons appear in the region 120-140 ppm.

Table 2-6: Infrared Data For Hydrido Complexes

Compound	ν(RuH)[a] (cm^{-1})	ν(RuCl)[b] (cm^{-1})
$RuHCl(\eta^6\text{-}C_6Me_6)(AsPh_3)$	1925	296
$RuHCl(\eta^6\text{-}C_6Me_6)(SbPh_3)$	1900	298
$RuHCl(\eta^6\text{-}C_6Me_6)(P[OPh]_3)$	1945	305
$RuHCl(\eta^6\text{-}C_6Me_6)(P[\underline{p}\text{-}C_6H_4F]_3)$	1955	302
$RuHCl(\eta^6\text{-}C_6Me_6)(P[\underline{p}\text{-}C_6H_4CH_3]_3)$	1955	302
$RuHCl(\eta^6\text{-}C_6Me_6)(P[\underline{p}\text{-}C_6H_4OCH_3]_3)$	1920	292
$RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2\underline{o}\text{-Tol})$	1935	(287,302)[c]
$RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tPh_2)$	1965	292
$RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2Pr^n)$	1923	294(br)
$RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2Pr^i)$	1940	295
$RuHCl(\eta^6\text{-}C_6Me_6)(PEtPh_2)$	1900	299
$RuHCl(\eta^6\text{-}C_6Me_6)(PMePh_2)$	1900	304
$RuHCl(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$	1880(br)	297

Table 2-6: Infrared Data For Hydrido Complexes (Cont'd)

Compound	ν(RuH)[a] (cm^{-1})	ν(RuCl)[b] (cm^{-1})
$RuHCl(\eta^6\text{-}C_6Me_6)(PMe_3)$	1935	279
$RuHCl(\eta^6\text{-}C_6Me_6)(P[OMe]_3)$	1950	
$RuHCl(\eta^6\text{-}C_6Me_6)(PEt_3)$	1925	300
$RuHCl(\eta^6\text{-}C_6Me_6)(PPr^i_3)$	1980	295
$RuHCl(\eta^6\text{-}C_6Me_6)(PCy_3)$	2010	287
$RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$	1960	298
$RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Me)$	2025	298(br)
$RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$	1997	
$RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Pr^n)$	2020	
$RuH_2(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$	1915(br)	
$RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$	1935(v br)	
$RuH_2(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$	1955, 1990	

a: KBr disc, peaks usually medium to strong; br = broad. b: Polythene disc; peaks ususally medium intensity.

c: It is not clear whether only one peak is due to ν(RuCl) or whether there is a solid state splitting effect.

The $^{31}P[^{1}H]$ NMR spectra of the hydrides showed a single resonance in the region δ 5-70ppm which was downfield from the corresponding dichloride by 5 to 30ppm, depending on the phosphine. The $^{31}P[^{1}H]$ NMR spectra of $RuHCl(\eta^6\text{-}C_6Me_6)(P[OR]_3)$ showed singlets at 153.5ppm {R = Me} and 135.7ppm {R = Ph} respectively, which were 30ppm downfield from the corresponding dichlorides. The ^{1}H NMR spectra of the hydrides displayed a resonance in the region δ -7 to -10ppm due to the hydride ligand with a doublet coupling to phosphorus of 50-65Hz. The methyl resonance of the co-ordinated hexamethylbenzene appeared as a sharp singlet upfield of free hexamethylbenzene {δ = 2.12ppm in C_6D_6} by up to 0.6ppm. The protons of the alkyl substituents of the phosphine ligands showed characteristic couplings to phosphorus {$^{2}J_{PH}$ ≈ 7 to 10Hz, $^{3}J_{PH}$ ≈ 12 to 15Hz}.

The chlorohydrido complexes presumably have a typical half-sandwich structure {Figure 2-2}, similar to the structurally characterized complex $RuCl_2(\eta^6\text{-}C_6H_6)(PMePh_2)$ [1].[23] The metal atom of the chlorohydrido adducts bears four different ligands in a pseudo-tetrahedral arrangement, hence the complexes are chiral. Thus the adducts containing $PBu^{t}Me_2$ and PMe_2Ph have diastereotopic methyl groups with quite distinet chemical shifts {see Table 2-4}. Similarly, diastereotopic methyl protons were observed for isopropyl groups in the chlorohydrides containing PPh_2Pr^{i} and PPr^{i}_3, and the t-butyl groups of the compounds containing PBu^{t}_2R {R = Me, Et, Pr^{n}}. Diastereotopic methylene protons of the ethyl and propyl groups in the

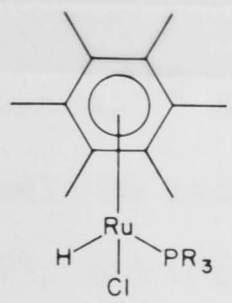


Figure 2-2: Structure of Chlorohydrido Complexes.

complexes bearing $PEtPh_2$, PPh_2Pr^n, PBu^t_2Et and $PBu^t_2Pr^n$ were also observed. All diastereotopic groups had distinct chemical shifts and coupling constants to phosphorus.

The mass spectra of most of the $RuHCl(\eta^6\text{-}C_6Me_6)L$ complexes showed parent ions consisting of broad clusters due to the seven isotopes of ruthenium and two of chlorine. The complexes containing $AsPh_3$ and $SbPh_3$ did not show parent ions, probably because they decomposed under the instrumental conditions. An interesting feature of the mass spectra of the hydrides is that the first fragment lost was always HCl.

The hydride complexes $RuHCl(\eta^6\text{-}C_6Me_6)L$ ($L = PBu^t_2Pr^n$, $AsPh_3$, $SbPh_3$) were temperature-sensitive. Thus, $RuHCl(\eta^6\text{-}C_6Me_6)(AsPh_3)$ decomposed when it was heated to reflux in toluene, and $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Pr^n)$ and $RuHCl(\eta^6\text{-}C_6Me_6)(SbPh_3)$ decomposed on prolonged heating in 2-propanol. Dichloromethane solutions of $RuHCl(\eta^6\text{-}C_6Me_6)(SbPh_3)$ decomposed on standing, whereas other complexes of the type $RuHCl(\eta^6\text{-}C_6Me_6)L$ were apparently stable in CH_2Cl_2 {for example, $RuHCl(\eta^6\text{-}C_6Me_6)(AsPh_3)$ was recrystallized from CH_2Cl_2/Et_2O}. The thermal instability of these complexes was probably because the ligands $PBu^t_2Pr^n$, $AsPh_3$ and $SbPh_3$ were weakly bound.

Synthesis of the Chlorohydrido Complexes

Method A

In his Ph.D. thesis,[165] A.K. Smith reported that $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ could be made in 59% yield by heating $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ and triphenylphosphine with sodium carbonate in aqueous 2-propanol. Later, Tai-Nang Huang[16,97] claimed that $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ could be prepared in 98% yield by heating $RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_3)$ with sodium carbonate in aqueous 2-propanol, but

subsequent attempts to repeat this synthesis resulted in low yields. However, it was found that yields of 65-80% of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ could be achieved by heating $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ with an excess of triphenylphosphine and sodium carbonate in anhydrous 2-propanol. Indeed, anhydrous conditions were required for the synthesis of $RuHCl(\eta^6\text{-}C_6Me_6)(PPr^i_3)$ by this method. When aqueous 2-propanol was used, the main product was the known complex $\{[Ru(\eta^6\text{-}C_6Me_6)]_2(\mu\text{-}OH)_3\}Cl$.[6] This species was also formed from the reaction between $RuCl_2(\eta^6\text{-}C_6Me_6)(PPr^i_3)$ and sodium carbonate in aqueous 2-propanol.

The synthesis of the hexamethylbenzene complexes $RuHCl(\eta^6\text{-}C_6Me_6)L$ by heating $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ with an excess of ligand and sodium carbonate in anhydrous 2-propanol {Method A} was limited in scope. Attempts to prepare $RuHCl(\eta^6\text{-}C_6Me_6)(P[\underline{p}\text{-}C_6H_4X]_3)$ {X = Me, OMe} by this method resulted in extensive arene displacement, and there was also some evidence of this in the synthesis of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2Pr^i)$. However, it was found that this method could be used satisfactorily for the synthesis of the complexes $RuHCl(\eta^6\text{-}C_6Me_6)L$ in which L had a larger cone angle or was less nucleophilic than PPh_3. This method was found to be satisfactory for L = PPh_2Pr^i, $PBu^t Ph_2$, PPr^i_3, PCy_3, PBu^t_2Me, PBu^t_2Et, $PBu^t_2Pr^n$, $P(\underline{p}\text{-}C_6H_4F)_3$, $AsPh_3$ and $SbPh_3$. These ligands, for either steric or electronic reasons, did not readily displace the hexamethylbenzene ring, whereas a large excess of the ligands $P(\underline{p}\text{-}C_6H_4X)_3$ {X = Me, OMe} readily displaced hexamethylbenzene from the initially formed hydride. The complex $RuHCl(\eta^6\text{-}C_6Me_6)(P[\underline{p}\text{-}C_6H_4CH_3]_3)$ could only be prepared by using a slight (6%) excess of ligand. Attempts to prepare $RuHCl(\eta^6\text{-}C_6Me_6)(P[\underline{p}\text{-}C_6H_4OCH_3]_3)$ by use of a 6% excess of $P(\underline{p}\text{-}C_6H_4OCH_3)_3$ gave an impure product.

Method B

Good yields {60-75%} of the hydrides $RuHCl(\eta^6\text{-}C_6Me_6)L$ {L = PBu^tPh_2, PBu^tMe_2, PMe_3} were obtained by heating the dichloro complexes $RuCl_2(\eta^6\text{-}C_6Me_6)L$ with sodium carbonate in anhydrous 2-propanol {Method B}. In the case of L = PBu^tPh_2, the yield {60%} was comparable with that obtained by heating $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ with an excess of PBu^tPh_2 and sodium carbonate in anhydrous 2-propanol {Method A}. However, method B was not generally useful. Long reaction times were required to obtain appreciable yields of $RuHCl(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$ and $RuHCl(\eta^6\text{-}C_6Me_6)(P[\underline{p}\text{-}C_6H_4OCH_3]_3)$ {38 and 60 hours respectively}. Yields of $RuHCl(\eta^6\text{-}C_6Me_6)(PEtPh_2)$ obtained by this method were very low {less than 15%}.

The speed with which $RuCl_2(\eta^6\text{-}C_6Me_6)(PBu^tPh_2)$ reacted to form the hydride suggests that phosphine dissociation may be an important step in the formation of the hydride {$RuCl_2(\eta^6\text{-}C_6Me_6)(PBu^tPh_2)$ was appreciably dissociated in solution, see above}. Heating of $RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_2\underline{o}\text{-Tol})$ with sodium carbonate in 2-propanol did not generate $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2\underline{o}\text{-Tol})$ but gave instead the cyclometallated complex $\overline{RuCl(\underline{o}\text{-}CH_2C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$ [26]. {This will be discussed further below}.

Methods C and D: Triphenylarsine and Triphenylstibine Displacement Reactions

A useful route for the preparation of $RuHCl(\eta^6\text{-}C_6Me_6)(PR_3)$ for a wide range of phosphorus donors was displacement of the triphenylarsine or triphenylstibine ligand under mild conditions from $RuHCl(\eta^6\text{-}C_6Me_6)(EPh_3)$ {E = As, Sb}. This type of synthesis has found surprisingly little application. When $\underline{cis}\text{-}PtCl_2(AsPh_3)_2$ was treated with PCy_3 and hydrazine hydrate in ethanol, $\underline{trans}\text{-}PtHCl(PCy_3)_2$ was

formed.[128] Similar treatment of cis-$PtCl_2(AsPh_3)_2$ with PPr^i_3 or PCy_2Ph formed trans-$PtCl_2(PR_3)_2$. More recently, it was reported that PMe_3, when present in excess, quantitatively displaced $AsMe_3$ from the adducts $MoCl_2(CO)_2(AsMe_3)_2(PMe_3)$, $[WCl_2(CO)_3(AsMe_3)]_2$ and $WBr_2(CO)_3(PMe_3)(AsMe_3)$, giving the compounds $MoCl_2(CO)_2(PMe_3)_3$, $WCl_2(CO)_2(PMe_3)_3$ and $WBr_2(CO)_2(PMe_3)_3$.[171]

When $RuHCl(\eta^6\text{-}C_6Me_6)(AsPh_3)$ was heated with 1.6 equivalents of $PEtPh_2$ in toluene at 70° for 14 hours, there was quantitative conversion to $RuHCl(\eta^6\text{-}C_6Me_6)(PEtPh_2)$. The order of ease of ligand displacement is $SbPh_3 > AsPh_3 >> PPh_3$. Heating of $RuHCl(\eta^6\text{-}C_6Me_6)(EPh_3)$ with 1.1 equivalents of $PEtPh_2$ for 15 hours at 70° resulted in no reaction for E = P, whilst for E = As there was 60% conversion, and for E = Sb conversion was 90%. These figures were only approximate, as both the arsine and stibine complex have limited solubility in benzene, and there was some undissolved material in the NMR samples. The reaction conditions were critical: if the temperature was not high enough, the reaction did not proceed to completion; if it was too high, arene displacement or thermal decomposition occurred. Similarly, when too little phosphine was used, the reaction was incomplete, whereas excessive phosphine displaced the arene. In general, heating of $RuHCl(\eta^6\text{-}C_6Me_6)(EPh_3)$ with 1.5 to 2.5 equivalents of ligand in toluene at 70-75° for 14-16 hours gave quantitative conversion. This method proved particularly useful for the synthesis of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2\underline{o}\text{-Tol})$, which could not be prepared by other means.

Pyridine and tri-ortho-tolylphosphine did not react with $RuHCl(\eta^6\text{-}C_6Me_6)(SbPh_3)$, and only 40% conversion occurred with 2 equivalents of $PBu^t_2Pr^n$. On the other hand, reaction of

$RuHCl(\eta^6\text{-}C_6Me_6)(SbPh_3)$ with diphenyl(2-vinylphenyl)phosphine or tris(pentafluorophenyl)phosphine gave products which did not contain hydride. Trimethylphosphine reacted with $RuHCl(\eta^6\text{-}C_6Me_6)(SbPh_3)$ to give the desired product together with about 20% of another hydride containing product {$\delta(Ru\underline{H}) = -8.44$ (d, $^2J_{PH} = 26.8Hz$)}.

The choice between $RuHCl(\eta^6\text{-}C_6Me_6)(AsPh_3)$ or $RuHCl(\eta^6\text{-}C_6Me_6)(SbPh_3)$ as starting material depended on the properties of the product. For example, treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(SbPh_3)$ with $PMePh_2$ gave a product which was very difficult to purify, presumably due to contamination by both $SbPh_3$ and PMe_2Ph. The product $RuHCl(\eta^6\text{-}C_6Me_6)(PMePh_2)$ was readily prepared and purified by starting from the arsine adduct, presumably because $AsPh_3$ was much more soluble in n-hexane. Generally, if the product $RuHCl(\eta^6\text{-}C_6Me_6)L$ was very soluble in toluene, then $RuHCl(\eta^6\text{-}C_6Me_6)(AsPh_3)$ was the more suitable starting material. However, $RuHCl(\eta^6\text{-}C_6Me_6)(AsPh_3)$ was much more difficult to handle than $RuHCl(\eta^6\text{-}C_6Me_6)(SbPh_3)$, because it was a very light, highly electrostatic feathery powder. In general, $RuHCl(\eta^6\text{-}C_6Me_6)(SbPh_3)$ was the hydride precursor of choice because of the ease of handling of the adduct and the greater lability of the stibine ligand.

Other Synthetic Methods

A number of attempts were made to find alternative syntheses for $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$, in the hope of finding a new general synthesis for $RuHCl(\eta^6\text{-arene})(PR_3)$. The mechanism of formation of $RuHCl(\eta^6\text{-}C_6Me_6)L$ from $RuCl_2(\eta^6\text{-}C_6Me_6)L$ by heating with sodium carbonate in 2-propanol is believed to be as follows. In the presence of sodium carbonate, a small amount of 2-propoxide is formed, which then displaces a chloro ligand from $RuCl_2(\eta^6\text{-}C_6Me_6)L$. Subsequent

β-elimination of acetone would then form the hydride ligand.[80] Thus reactions potentially generating 2-propoxide were initially studied.

There was no apparent reaction between $RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_3)$ and triethylamine in 2-propanol; in contrast, the analogous osmium complex $OsCl_2(\eta^6\text{-}\underline{p}\text{-}C_6H_4MePr^i)(PPr^i_3)$ formed $OsHCl(\eta^6\text{-}\underline{p}\text{-}C_6H_4MePr^i)(PPr^i_3)$ on reaction with triethylamine in ethanol.[40] The hydride $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ was detected by ^1H NMR spectroscopy among the products of the reaction of $RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_3)$ with sodium 2-propoxide, but it was not isolated. Treatment of $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ with an excess of sodium 2-propoxide and an excess of PPh_3 resulted in decomposition. However, when this reaction was carried out using two equivalents of sodium 2-propoxide and two equivalents of PPh_3, $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ was isolated in 20% yield. The reaction between $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$, an excess of sodium hydroxide and triphenylphospine in 2-propanol led to a mixture of products, including the known cyclometallated species $\overline{RuH(\underline{o}\text{-}C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$ [27].[14,97]

Treatment of $MX_2(\eta^6\text{-}C_6H_6)(PR_3)$ with zinc dust in methanol was reported to give $MHX(\eta^6\text{-}C_6H_6)(PR_3)$ {M = Ru, X = Cl, O_2CCF_3, R not specified; M = Os, X = I, R = Me, Pr^i}.[182] However, the reaction between $RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_3)$ and zinc dust in 2-propanol formed an unidentified yellow powder. The complex $RuHCl(PPh_3)_3$[86] was the product of the reaction between $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$, zinc dust and excess PPh_3 in 2-propanol.

It was reported that the reaction of $RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_3)$ with sodium borohydride in THF afforded $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ in 45% yield.[16] Similarly, the isoelectronic $IrCl_2(\eta^5\text{-}C_5Me_5)(PMe_3)$, when

treated with 1.5 equivalents of sodium borohydride in 2-propanol, gave $IrHCl(\eta^5\text{-}C_5Me_5)(PMe_3)$.[100] In contrast, there was no apparent reaction when $RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_3)$ was treated with 1.5 equivalents of sodium borohydride in 2-propanol for over sixty hours at room temperature. Heating of this mixture with an excess of sodium borohydride gave primarily the known dihydride $RuH_2(\eta^6\text{-}C_6Me_6)(PPh_3)$[180] and some $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$. It was thought that replacement of one of the chloro ligands from $RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_3)$ by a more labile ligand such as acetate might permit the reaction with sodium borohydride to proceed under milder conditions, and so avoid formation of the dihydride. Treatment of $RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_3)$ with one equivalent of silver acetate followed by one equivalent of sodium borohydride gave $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ in 25% isolated yield. Unfortunately, the product from this reaction could not consistently be obtained in a pure state, and no further work was done with this method.

Arenes Other Than Hexamethylbenzene

In general, attempts to prepare other arene ruthenium hydrides of the type $RuHCl(\eta^6\text{-arene})(PPh_3)$ by heating $[RuCl_2(\eta^6\text{-arene})]_2$ with an excess of triphenylphosphine and sodium carbonate in 2-propanol were unsuccessful, because the arenes were too easily displaced. Thus, heating of $[RuCl_2(\eta^6\text{-}1,2,4,5\text{-}C_6H_2Me_4)]_2$ with 2.5 equivalents triphenylphosphine and sodium carbonate in 2-propanol resulted in only a 7% yield of the desired complex, $RuHCl(\eta^6\text{-}1,2,4,5\text{-}C_6H_2Me_4)(PPh_3)$, the main product being $RuHCl(PPh_3)_3$.[86] The sole product formed by the reaction of $[RuCl_2(\eta^6\text{-}C_6H_3Me_3)]_2$ with excess triphenylphosphine and sodium carbonate in 2-propanol was $RuHCl(PPh_3)_3$.

However, excess triisopropylphosphine apparently did not displace benzene during the synthesis of $RuCl_2(\eta^6\text{-}C_6H_6)(PPr^i_3)$.

Treatment of $[RuCl_2(\eta^6\text{-}C_6H_6)]_2$ with an excess of PPr^i_3 and sodium carbonate in 2-propanol gave a mixture, which, on chromatography gave the desired complex $RuHCl(\eta^6\text{-}C_6H_6)(PPr^i_3)$, although in only 4% isolated yield. There was also a second unidentified product, which showed a strong sharp peak at $1905cm^{-1}$ in the infrared spectrum. The ^1H NMR spectrum displayed two co-ordinated benzene resonances in the ratio 1:2 at δ 5.33 and 5.03ppm, as well as PPr^i_3 resonances. The highest mass peak in the mass spectrum was at m/z = 487, which did not correspond to any obvious fragment. The apparent stability of $RuHCl(\eta^6\text{-}C_6H_6)(PPr^i_3)$ suggests that bulky phosphines will form stable benzeneruthenium hydrido complexes $RuHCl(\eta^6\text{-}C_6H_6)L$, but no further work has been done with these compounds.

3) THE BASE MEDIATED CYCLOMETALLATION OF DIPHENYL-ortho-TOLYLPHOSPHINE

Heating of $RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_2\underline{o}\text{-Tol})$ with sodium carbonate in 2-propanol gave the cyclometallated complex $\overline{RuCl(\underline{o}\text{-}CH_2C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$ [26]. The structure of this species {Figure 2-3} was assigned by spectroscopic methods. The ^1H NMR spectrum in CD_2Cl_2 showed diastereotopic methylene protons at δ 3.16ppm (dd, $^2J_{H^aH^b}$ = 13.3Hz, $^3J_{PH^a}$ = 5.9Hz) and δ 3.33ppm (br d, $^3J_{PH^b}$ small). There was a singlet at δ 1.76ppm due to co-ordinated C_6Me_6, and a small broad peak at δ 1.53ppm, which was probably due to an impurity. The intensity of the signal at δ 1.53ppm corresponded to approximately three protons, whilst the hexamethylbenzene resonance integrated to approximately sixteen protons {eighteen were expected}.

The ^{31}P resonance of $\overline{RuCl(\underline{o}\text{-}CH_2C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$ occurred at δ 62.1ppm, 30ppm downfield from the resonance due to

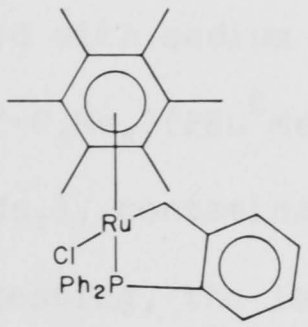


Figure 2-3: The structure of [26]

$RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_2\underline{o}\text{-Tol})$, which was consistent with the presence of a five-membered ring.[67] The mass spectrum showed the expected parent ion at m/z 574, although the highest mass peaks were at m/z 618 and 620. The latter are believed to be due to the bromo analogue $\overline{RuBr(\underline{o}\text{-}CH_2C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$, formed by exchange with adventitious bromide ions in the mass spectrometer {the so-called memory effect}.[22,118,119] The molecular weight by vapour pressure osmometry in dichloromethane was found to be 578 {required 574}. Final proof of the structure of $\overline{RuCl(\underline{o}\text{-}CH_2C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$ was obtained by treatment of $\overline{RuCl(\underline{o}\text{-}CH_2C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$ with sodium borohydride. The product formed was $\overline{RuH(\underline{o}\text{-}CH_2C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$, which was spectroscopically identical with the product prepared from the reaction of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2\underline{o}\text{-Tol})$ with methyllithium {see Chapter 3}.

4) DIHYDRIDO COMPLEXES

In the course of this work, it was decided to characterize the dihydrido complexes $RuH_2(\eta^6\text{-}C_6Me_6)(PR_3)$ (PR_3 = PMe_2Ph, PBu^tMe_2, PBu^t_2Et) because it was suspected that they were being formed as by-products in some of the cyclometallation reactions to be discussed in Chapter 3. They were readily prepared by heating the appropriate

dichloro or chlorohydrido adducts with sodium borohydride in 2-propanol. When treated with sodium borohydride in 2-propanol at room temperature, $RuCl_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ reacted rapidly to form $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$, contaminated with approximately 15% $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$. On heating, the latter was formed in 51% isolated yield. The previously characterized dihydrides $RuH_2(\eta^6\text{-}C_6Me_6)L$ {L = PMe_3, $PMePh_2$, PPh_3}[180] were also readily prepared by this method.

The dihydrides were pale yellow to white air-sensitive powders, which decomposed on contact with air over an hour in the solid state, and very rapidly in solution, turning black. The dihydrides showed $^{31}P[^1H]$ NMR resonances to slightly lower field than those of the corresponding $RuHCl(\eta^6\text{-}C_6Me_6)L$ complexes. These signals appeared as triplets on allowing selective coupling to the hydride protons, thus confirming the presence of two hydride ligands. The hydride chemical shifts of the dihydrides were shifted more than 1ppm to higher field than those of the corresponding chlorohydrides, and the coupling to phosphorus was reduced to approximately 45Hz. Protons which were diastereotopic in the chlorohydrido complexes were equivalent in the ^1H NMR spectra of the analogous dihydrides, as expected, since the latter were achiral molecules. In the infrared spectra, a band due to ν(RuH) appeared in the region 1900-2000cm^{-1}.

EXPERIMENTAL

All manipulations were carried out in an atmosphere of purified nitrogen or argon using conventional Schlenk techniques. All solvents were freshly degassed by distillation under nitrogen prior to use. Diethyl ether, THF, toluene and benzene were dried by

distillation from sodium benzophenone ketyl, and 2-propanol was dried by distillation from calcium hydride. Chromatography was performed under nitrogen using degassed neutral alumina {Brockman activity 3}. Tertiary phosphines were either prepared by standard methods or used as received from commercial suppliers. Sodium borohydride was recrystallized from diglyme.[149] Literature procedures were used for the preparation of $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$,[15] $[RuCl_2(\eta^6\text{-}1,2,4,5\text{-}C_6H_2Me_4)]_2$,[21] $[RuCl_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]_2$,[24] $[RuCl_2(\eta^6\text{-}C_6H_6)]_2$,[190] $RuCl_2(\eta^6\text{-}C_6Me_6)(PMe_3)$,[180] $RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_2\underline{o}\text{-Tol})$,[97] $RuCl_2(\eta^6\text{-}C_6Me_6)(P[\underline{p}\text{-}C_6H_4OCH_3]_3)$ and $RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_3)$.[14,97]

The following instruments were used for spectroscopic measurements: ^1H NMR: Varian HA100, Jeol FX200, Bruker CXP200; ^{31}P NMR: Bruker B-KR 322S (24.29 MHz), Bruker CXP200 (80.98 MHz), Jeol FX60 (24.21 MHz); ^{13}C NMR: Jeol FX200 (50.10 MHz); ^{19}F NMR: Bruker CXP200 (188.15 MHz); IR: Perkin-Elmer 683 (4000-200cm^{-1}), Hitachi FIS-3 (400-30cm^{-1}); mass spectra: VG Micromass 7070F (70eV). Analyses and molecular weight determinations were carried out by the ANU Microanalytical Unit. NMR chemical shift data are quoted with respect to TMS (^1H and ^{13}C NMR), 85% H_3PO_4 (^{31}P NMR) and $CFCl_3$ (^{19}F NMR), with values to low frequency of the reference being negative.

The preparation of the complex $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ has been described previously,[97,165] however, the method described below is an improvement. The preparation of $RuCl_2(\eta^6\text{-}C_6H_6)(PPr^i_3)$ was described independently during the course of this work.[181]

1) PREPARATION OF DICHLORO COMPLEXES

Preparation of $RuCl_2(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$

A suspension of $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ (1.252g, 1.873mmol) was heated to reflux with PMe_2Ph (0.65ml, 4.55mmol) in 2-propanol (30ml) for 3h. The solvent was removed under reduced pressure and the residue was recrystallized from chloroform/diethyl ether, yielding deep red crystals of $RuCl_2(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$ (1.42g, 3.0 mmol, 80%).

The following were prepared similarly from $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ and the appropriate phosphine (yields in parentheses): $RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_2Et)$ (fine pink powder, 73%); $RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_2\underline{o}\text{-}Tol).CHCl_3$ [25] (fine pink powder, 72%); $RuCl_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ (from CH_2Cl_2/Et_2O, 71%); $RuCl_2(\eta^6\text{-}C_6Me_6)(P[OMe]_3)$ (from CH_2Cl_2/Et_2O, 48%).

The complex $RuCl_2(\eta^6\text{-}1,2,4,5\text{-}C_6H_2Me_4)(PPh_3)$ was prepared similarly in 79% yield from $[RuCl_2(\eta^6\text{-}1,2,4,5\text{-}C_6H_2Me_4)]_2$ and PPh_3.

Preparation of $RuCl_2(\eta^6\text{-}C_6Me_6)(PBu^tPh_2)$

$RuCl_2(\eta^6\text{-}C_6Me_6)(PBu^tPh_2)$ was prepared by heating $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ to reflux with a fourfold excess of PBu^tPh_2 in 2-propanol for 4h. Recrystallization from chloroform/ether gave $RuCl_2(\eta^6\text{-}C_6Me_6)(PBu^tPh_2)$ as orange crystals in 56% yield.

The following complexes were prepared similarly using $[RuCl_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]_2$ and the appropriate phosphine (yields in parentheses): $RuCl_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PBu^tPh_2)$ (63%), $RuCl_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PCy_3)$ (6%) and $RuCl_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PPr^i_3)$ (pink feathery crystals, 11%). The following were prepared in an analogous manner

Table 2-7: Analytical Data for Dichloro Complexes

Calculated figures in parentheses.

Compound	C	H	Cl	P
$RuCl_2(\eta^6\text{-}C_6H_6)(PBu^tPh_2).CHCl_3$	44.50 (45.16)	4.16 (4.28)	28.50 (28.98)	5.71 (5.06)
$RuCl_2(\eta^6\text{-}C_6H_6)(PCy_3).0.3CH_2Cl_2$ [a]	52.62 (52.49)	7.26 (7.18)	16.68 (16.59)	5.44 (5.57)
$RuCl_2(\eta^6\text{-}C_6H_6)(PPr^i_3)$	42.63 (43.91)	6.46 (6.63)	18.00 (17.28)	7.36 (7.55)
$RuCl_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PBu^tPh_2).0.5CHCl_3$	52.62 (51.55)	5.32 (5.34)	21.11 (20.88)	5.22 (5.21)
$RuCl_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(PPr^i_3)$	47.56 (47.79)	7.31 (7.35)	15.70 (15.67)	6.77 (6.85)
$RuCl_2(\eta^6\text{-}1,2,4,5\text{-}C_6H_2Me_4)(PPh_3)$	59.12 (59.16)	5.14 (5.14)	12.71 (12.47)	5.25 (5.45)
$RuCl_2(\eta^6\text{-}C_6Me_6)(PPr^i_3)$ [b]	51.04 (51.01)	7.98 (7.95)	14.27 (14.34)	6.35 (6.26)
$RuCl_2(\eta^6\text{-}C_6Me_6)(PBu^tPh_2)$	57.51 (58.33)	6.36 (6.47)	12.27 (12.30)	5.51 (5.37)
$RuCl_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$	48.25 (47.79)	7.18 (7.35)	15.49 (15.67)	6.94 (6.85)
$RuCl_2(\eta^6\text{-}C_6Me_6)(PEtPh_2)$	56.77 (56.93)	6.18 (6.06)	13.20 (12.93)	5.91 (5.65)
$RuCl_2(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$	50.69 (50.85)	6.25 (6.19)	15.82 (15.01)	6.96 (6.56)
$RuCl_2(\eta^6\text{-}C_6Me_6)(P[OMe]_3).0.4CH_2Cl_2$	37.37 (37.57)	5.83 (5.69)	18.62 (20.16)	6.80 (6.29)
$RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_2\underline{o}\text{-Tol}).CHCl_3$	52.35 (52.66)	4.99 (4.97)	19.23 (24.28) [c]	

a: Ru 18.17 (18.18)

b: Ru 20.44 (20.44)

c: See text for explanation.

from $[RuCl_2(\eta^6\text{-}C_6H_6)]_2$ and the appropriate phosphine: $RuCl_2(\eta^6\text{-}C_6H_6)(PBu^tPh_2)$ (70%); $RuCl_2(\eta^6\text{-}C_6H_6)(PCy_3)$ (benzene reaction medium, recrystallized from CH_2Cl_2/Et_2O, 18%); and $RuCl_2(\eta^6\text{-}C_6H_6)(PPr^i_3)$ (benzene reaction medium, recrystallized from CH_2Cl_2/Et_2O, 18%).

Preparation of $RuCl_2(\eta^6\text{-}C_6Me_6)(PPr^i_3)$

The compound $RuCl_2(\eta^6\text{-}C_6Me_6)(PPr^i_3)$ was prepared by heating $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ with a fivefold excess of PPr^i_3 in 2-propanol for six hours. The solution was allowed to cool, and, after being filtered, was set aside overnight in a freezer. The precipitate was filtered and washed with ether leaving fine orange crystals of $RuCl_2(\eta^6\text{-}C_6Me_6)(PPr^i_3)$ in 26% yield.

2) PREPARATION OF CHLOROHYDRIDO COMPLEXES

Hexamethylbenzene Chlorohydrido Complexes

METHOD A : $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2 + L + Na_2CO_3$ in refluxing 2-propanol for 15 hours. See Table 2-3 for the mole ratio of ligand to ruthenium used in each case.

Preparation of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$

A suspension of $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ (0.45g, 0.67 mmol), PPh_3 (0.9g, 3.4mmol) and powdered anhydrous sodium carbonate (0.45g, 4.2mmol) were heated to reflux in 2-propanol (30ml) for 15 hours. The yellow suspension was allowed to cool and was evaporated to dryness under reduced pressure. The residue was extracted with toluene (ca. 50ml). The toluene extract was evaporated to approximately half volume and addition of n-hexane yielded $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ as an air-sensitive microcrystalline yellow powder (0.50g, 0.89mmol, 65%).

The following were prepared similarly from $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$, the appropriate phosphine and excess sodium carbonate in 2-propanol (yields in parentheses): $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t Ph_2)$ (60%); $RuHCl(\eta^6\text{-}C_6Me_6)(PCy_3)$ (57%); $RuHCl(\eta^6\text{-}C_6Me_6)(PPr^i_3)$ (58%); $RuHCl(\eta^6\text{-}C_6Me_6)(P[\underline{p}\text{-}C_6H_4F]_3)$ (68%); $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2Pr^i)$ (65%); $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Me)$ (64%); $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$ (43%).

The complexes $RuHCl(\eta^6\text{-}C_6Me_6)(AsPh_3)$, $RuHCl(\eta^6\text{-}C_6Me_6)(SbPh_3)$ and $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Pr^n)$ were prepared similarly, but the reaction mixtures were heated for only three hours. $RuHCl(\eta^6\text{-}C_6Me_6)(AsPh_3)$ was extracted with dichloromethane and precipitated with ether (80% yield). $RuHCl(\eta^6\text{-}C_6Me_6)(SbPh_3)$ was extracted with THF and precipitated with n-hexane (75% yield). $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Pr^n)$ was extracted with toluene, and the extract evaporated under reduced pressure to a small volume. The extract was then loaded onto an alumina column prepared with n-hexane, and was eluted with n-hexane. The eluate was discarded. The column was then eluted with dichloromethane and the subsequent eluate was evaporated to dryness under reduced pressure. The residue was recrystallized from toluene/n-hexane forming fine orange crystals of $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Pr^n)$ in 21% yield. Both $RuHCl(\eta^6\text{-}C_6Me_6)(SbPh_3)$ and $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Pr^n)$ decomposed on prolonged heating.

$RuHCl(\eta^6\text{-}C_6Me_6)(P[\underline{p}\text{-}C_6H_4CH_3]_3)$ was prepared by using only a 6% excess of $P[\underline{p}\text{-}C_6H_4CH_3]_3$ (46% yield).

Table 2-8: Analytical Data for Hydrido Complexes

Calculated figures in parentheses.

Compound	MW[a]	C	H	Cl	P
$RuHCl(\eta^6\text{-}C_6Me_6)(AsPh_3)$		59.07 (59.46)	5.42 (5.65)	5.89 (5.85)	12.64(12.36)[b]
$RuHCl(\eta^6\text{-}C_6Me_6)(SbPh_3)$		54.87 (55.19)	5.25 (5.30)	5.18 (5.43)	18.55(18.64)[c]
$RuHCl(\eta^6\text{-}C_6Me_6)(P[OPh]_3)$	610	58.93 (59.06)	5.62 (5.83)	5.09 (5.81)	5.12 (5.08)
$RuHCl(\eta^6\text{-}C_6Me_6)(P[\underline{p}\text{-}C_6H_4F]_3)$[d]	616	58.24 (58.49)	5.11 (5.07)	5.94 (5.75)	5.30 (5.03)
$RuHCl(\eta^6\text{-}C_6Me_6)(P[\underline{p}\text{-}C_6H_4CH_3]_3)$	604	66.40 (65.60)	6.67 (6.67)	5.51 (5.87)	5.59 (5.13)
$RuHCl(\eta^6\text{-}C_6Me_6)(P[p\text{-}C_6H_4OCH_3]_3)$	652	60.15 (60.78)	6.25 (6.18)	5.23 (5.44)	4.77 (4.75)
$RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2\underline{o}\text{-Tol})$	576	64.34 (64.63)	6.36 (6.30)	5.87 (6.15)	5.12 (5.38)
$RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tPh_2)$	542	61.45 (62.04)	7.12 (7.07)	6.10 (6.54)	5.65 (5.71)
$RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2Pr^n)$	528	61.35 (61.41)	6.91 (6.87)	6.88 (6.71)	5.92 (5.87)
$RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2Pr^i)$	528	60.88 (61.41)	6.73 (6.87)	6.86 (6.71)	6.09 (5.87)
$RuHCl(\eta^6\text{-}C_6Me_6)(PEtPh_2)$	514	60.33 (60.75)	6.77 (6.67)	6.96 (6.90)	6.29 (6.03)
$RuHCl(\eta^6\text{-}C_6Me_6)(PMePh_2)$	500	60.05 (60.05)	6.46 (6.45)	6.91 (7.09)	5.92 (6.19)
$RuHCl(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$	438	54.68 (54.85)	6.96 (6.90)	7.98 (8.10)	6.84 (7.07)

Table 2-8: Analytical Data for Hydrido Complexes (Cont'd)

Compound	MW[a]	C	H	Cl	P
$RuHCl(\eta^6\text{-}C_6Me_6)(PMe_3)$	376	47.69 (47.93)	7.85 (7.51)	9.46 (9.43)	8.30 (8.24)
$RuHCl(\eta^6\text{-}C_6Me_6)(P[OMe]_3)$	424	42.39 (42.50)	6.81 (6.66)	8.35 (8.36)	7.02 (7.31)
$RuHCl(\eta^6\text{-}C_6Me_6)(PEt_3)$	418	51.39 (51.73)	8.28 (8.20)	8.54 (8.48)	7.07 (7.41)
$RuHCl(\eta^6\text{-}C_6Me_6)(PPr^i_3)$	460	54.97 (54.83)	8.76 (8.76)	7.44 (7.71)	6.85 (6.73)
$RuHCl(\eta^6\text{-}C_6Me_6)(PCy_3)$	580	62.32 (62.10)	9.00 (9.03)	6.08 (6.11)	5.57 (5.34)
$RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$	418	52.90 (51.73)	8.51 (8.20)	8.60 (8.48)	7.65 (7.41)
$RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Me)$	460	53.95 (54.83)	9.10 (8.76)	7.67 (7.71)	6.33 (6.73)
$RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$	474[e]	55.98 (55.74)	9.44 (8.93)	7.47 (7.48)	6.29 (6.53)
$RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Pr^n)$	488	56.24 (56.60)	9.61 (9.09)	6.68 (7.26)	5.99 (6.35)
$RuH_2(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$	404	59.96 (59.53)	7.97 (7.74)		7.90 (7.68)
$RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$	384	56.68 (56.37)	9.39 (9.20)		8.32 (8.08)
$RuH_2(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$	440	60.97 (60.11)	10.23 (9.86)		7.55 (7.05)

a: Parent ion (^{102}Ru, ^{35}Cl) in 70eV mass spectrum b: As c: Sb d: F 8.99 (9.25)

e: Highest mass peak at m/z = 508 ($RuCl_2(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$)

METHOD B : $RuCl_2(\eta^6\text{-}C_6Me_6)L + Na_2CO_3$ in refluxing 2-propanol for 15h.

Preparation of $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$

A suspension of $RuCl_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ (2.62g, 5.79mmol) and anhydrous sodium carbonate (2.03g, 19.1mmol) in 2-propanol (50ml) was heated to reflux for 15h. The yellow solution was allowed to cool and was evaporated to dryness under reduced pressure. The residue was extracted with toluene, and the extract was reduced in volume. Addition of n-hexane gave large, deep brown crystals of $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ (1.80g, 4.30 mmol, 74%).

$RuHCl(\eta^6\text{-}C_6Me_6)(PMe_3)$ was prepared similarly (75% yield).

$RuHCl(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$ was prepared by heating $RuCl_2(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$ and excess sodium carbonate to reflux in 2-propanol for 38h. The solvent was evaporated under reduced pressure, and the residue was extracted with dichloromethane. The extract was reduced in volume, loaded onto an alumina column and eluted with dichloromethane. The yellow eluate was evaporated to dryness under reduced pressure and was recrystallized from toluene/n-hexane forming fine orange crystals of $RuHCl(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$ in 43% yield.

$RuHCl(\eta^6\text{-}C_6Me_6)(P[\underline{p}\text{-}C_6H_4OCH_3]_3)$ was prepared by heating $RuCl_2(\eta^6\text{-}C_6Me_6)(P[\underline{p}\text{-}C_6H_4OCH_3]_3)$ and excess sodium carbonate to reflux in 2-propanol for 60h. After removal of the solvent, the residue was suspended in toluene and the suspension was filtered through filter aid. The filtrate was evaporated under reduced pressure to small volume and n-hexane was added yielding fine yellow crystals of $RuHCl(\eta^6\text{-}C_6Me_6)(P[\underline{p}\text{-}C_6H_4OCH_3]_3)$ in 21% yield.

METHODS C AND D : $RuHCl(\eta^6\text{-}C_6Me_6)(EPh_3)$ + L in toluene at 70° for 16 hours {E = As, Sb}. See Table 2-3 for the mole ratio of ligand to ruthenium used in each case.

Preparation of $RuHCl(\eta^6\text{-}C_6Me_6)(PMePh_2)$

A suspension of $RuHCl(\eta^6\text{-}C_6Me_6)(AsPh_3)$ (1.54 g, 2.54 mmol) and $PMePh_2$ (1.2ml, 6.4mmol) in toluene (50 ml) was heated at 70-75° for 16h. The bright orange solution was cooled and evaporated to dryness under reduced pressure. The residue was recrystallized from toluene/n-hexane yielding fine orange crystals of $RuHCl(\eta^6\text{-}C_6Me_6)(PMePh_2)$ (0.99 g, 1.99mmol, 78%).

The following were prepared similarly (yields in parentheses): $RuHCl(\eta^6\text{-}C_6Me_6)(PEtPh_2)$ (65%); $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2Pr^n)$ (80%).

The following were prepared similarly from $RuHCl(\eta^6\text{-}C_6Me_6)(SbPh_3)$ and the appropriate ligand, and were recrystallized from toluene/n-hexane (yields in parentheses): $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2\underline{o}\text{-Tol})$ (66%); $RuHCl(\eta^6\text{-}C_6Me_6)(P[\underline{p}\text{-}C_6H_4OCH_3]_3)$ (40%); $RuHCl(\eta^6\text{-}C_6Me_6)(P[OPh]_3)$ (51%); $RuHCl(\eta^6\text{-}C_6Me_6)(PEt_3)$ (57%); $RuHCl(\eta^6\text{-}C_6Me_6)(P[OMe]_3)$ (32%).

Other Arene Chlorohydrido Complexes

Preparation of $RuHCl(\eta^6\text{-}1,2,4,5\text{-}C_6H_2Me_4)(PPh_3)$

A suspension of $[RuCl_2(\eta^6\text{-}1,2,4,5\text{-}C_6H_2Me_4)]_2$ (0.55g, 0.90mmol), PPh_3 (1.18g, 4.5mmol) and sodium carbonate (0.60g, 5.7mmol) were heated to reflux in 2-propanol (30ml) for 17h. The suspension was cooled and filtered. {The residue was discarded, as extraction with

toluene did not give the anticipated product}. The filtrate was evaporated to dryness under reduced pressure. The residue was recrystallized from toluene/n-hexane, yielding $RuHCl(\eta^6\text{-}1,2,4,5\text{-}C_6H_2Me_4)(PPh_3)$ as a yellow-brown solid (77mg, 0.14mmol, 7%). {Spectroscopic data: IR (KBr disc): $\nu(RuH) = 1935cm^{-1}$. ^1H NMR (C_6D_6): 6.9-8.0 (m, $C_6\underline{H}_5$); 4.29 ($C_6\underline{H}_2Me_4$); 1.90, 1.58 ($C_6H_2\underline{Me}_4$); -7.55 (d, $^2J_{PH}$ = 55Hz, Ru$\underline{H}$)}.

Preparation of $RuHCl(\eta^6\text{-}C_6H_6)(PPr^i_3)$

A suspension of $[RuCl_2(\eta^6\text{-}C_6H_6)]_2$ (0.51g, 1.0mmol), PPr^i_3 (1.0ml, 5mmol) and sodium carbonate (0.35g, 3.3mmol) was heated to reflux in 2-propanol (30ml) for sixteen hours. The suspension was evaporated to dryness under reduced pressure. The residue was suspended in dichloromethane and was loaded onto an alumina column cooled to -30°. The column was eluted with dichloromethane. The first fraction, brown-grey in colour, was discarded. The second fraction to elute, yellow in colour, was collected at -78°. The eluate was evaporated to dryness under reduced pressure at low temperature (ca. -40°), leaving a dark yellow oil. This was recrystallized from THF/n-hexane, yielding an orange yellow solid (0.042g). {Spectroscopic data: IR (KBr disc): Strong sharp peaks at 1905, 1910cm^{-1}, shoulder at 1930cm^{-1}. ^1H NMR (C_6D_6): 7.16 (free $C_6\underline{H}_6$); 5.33, 5.03 (co-ordinated $C_6\underline{H}_6$); 2.4-2.6 (m, C$\underline{H}Me_2$); 0.8-1.8 (m,CH$\underline{Me}_2$); no hydride resonance was observed between 0 and -15ppm. $^{1\,3}C[^1H]$ NMR (C_6D_6): Resonances at 25.1, 20.7, 19.9 and 16.5ppm. Mass spectrum: highest mass peak at m/z 486.6}. The yellow third fraction eluted almost immediately after the second. It was collected at -78° and was evaporated to dryness under reduced pressure at low temperature (below 0°). The residue was recrystallized from THF/n-hexane yielding golden-yellow crystals of $RuHCl(\eta^6\text{-}C_6H_6)(PPr^i_3)$ (0.034g, 91µmol, 4%). {Spectroscopic data: IR

(KBr disc): ν(RuH) = 1985cm^{-1} (broad, weak). ^{1}H NMR (C_6D_6): 4.92 ($C_6\underline{H}_6$); 1.7-2.2 (m, C$\underline{H}$Me$_2$); 0.9-1.2 (m, CH$\underline{Me}_2$); -7.14 (d, $^2J_{PH}$ = 51Hz, Ru$\underline{H}$). Mass spectrum: parent ion present at m/z 376}.

3) PREPARATION OF $\overline{RuCl(o\text{-}CH_2C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$ [26]

A suspension of $RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_2\underline{o}\text{-Tol})$ (0.50g, 0.82mmol) and sodium carbonate (0.40g, 0.38mmol) in 2-propanol (30ml) was heated to reflux for 15h. The yellow slurry was evaporated to dryness under reduced pressure. The residue was extracted with dichloromethane and the extract was reduced in volume. Addition of ether precipitated [26] as a fine yellow powder (0.24g, 0.42mmol, 51%). ^{1}H NMR (CD_2Cl_2): 1.53 {impurity?}, 1.76 ($C_6[C\underline{H}_3]_6$); 3.16 (dd, $^2J_{H_aH_b}$ = 13.3, $^3J_{PH}a$ = 5.9), 3.33 (br d, $^3J_{PH}b$ small) ($C\underline{H}_2$); 6.9-8.1 (m, $C_6\underline{H}_4$ and $C_6\underline{H}_5$). ^{31}P[^{1}H] NMR (CD_2Cl_2): δ(P) = 62.1. ^{13}C[^{1}H] NMR (CD_2Cl_2): 15.3 ($C_6[\underline{C}H_3]_6$); 31.1 ($\underline{C}H_2$). IR (KBr disc): ν(RuCl) = 306cm^{-1}. Analysis: $C_{31}H_{34}ClPRu.0.15CH_2Cl_2$ requires C 63.75, H 5.89, Cl 7.86, P 5.27; Found C 63.75, H 6.09, Cl 8.23, P 5.34. Parent ion present in mass spectrum at m/z = 574 {there were also peaks at m/z = 618, 620 due to "memory ion effect", see text}. MW 578 (required: 574) by vapour pressure osmometry in a 4.9mM CH_2Cl_2 solution.

4) PREPARATION OF DIHYDRIDO COMPLEXES

Preparation of $RuH_2(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$

A suspension of $RuCl_2(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$ (0.31g, 0.65mmol) and sodium borohydride (0.104g, 2.75mmol) in 2-propanol (10ml) was heated to reflux for 45min. The brown suspension was evaporated to dryness under reduced pressure and the residue was extracted with

toluene. The toluene extract was evaporated to dryness and dried under vacuum. The dried extract was sublimed at 105°/10^{-5}mm Hg, onto a probe at -20° to give $RuH_2(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$ as a very pale yellow powder (0.15g, 0.36mmol , 56%).

$RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ was prepared similarly (51% yield).

$RuH_2(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$ was prepared in an analogous manner from $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$ (63% yield).

CHAPTER 3

ALKYLATION AND CYCLOMETALLATION REACTIONS

Studies by Tai-Nang Huang[97] of the reactions of $RuCl_2(\eta^6$-arene)L with EtMgBr showed that either cyclometallated complexes of the type $\overline{RuH(C\sim PR_2)}(\eta^6$-arene) or zero-valent ruthenium ethylene complexes $Ru(\eta^6$-arene)$(\eta^2-C_2H_4)$L could be formed, the product depending on the nature of the arene and ligand L. For hexamethylbenzene complexes containing triarylphosphines or ligands of greater steric demand {eg. PPh_2Pr^i, PPh_2o-Tol}, treatment with EtMgBr was claimed to give the cyclometallated compounds, whilst the hexamethylbenzene complexes with less bulky ligands {eg. $P[OR]_3$, PBu^n_3, PPh_2Me} were reported to form ethylene complexes. Similar treatment of $RuCl_2(\eta^6$-1,3,5-$C_6H_3Me_3)(PPh_3)$ gave a 1:1 mixture of $\overline{RuH(o\text{-}C_6H_4PPh_2)}(\eta^6$-1,3,5-$C_6H_3Me_3)$ and $Ru(\eta^6$-$C_6H_3Me_3)(\eta^2-C_2H_4)(PPh_3)$, whereas the benzene analogue gave rise solely to the ethylene complex $Ru(\eta^6$-$C_6H_6)(\eta^2-C_2H_4)(PPh_3)$.

The cyclometallated complex $\overline{RuH(o\text{-}C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$ [27] was also prepared by treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ with methyllithium, phenyllithium or Red-Al $\{Na[AlH_2(OCH_2CH_2OCH_3)_2]\}$.[14,97] The path of the reaction between $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ and methyllithium was suggested to involve initial formation of an unstable methyl hydride which subsequently eliminated methane, yielding a zero-valent, co-ordinatively unsaturated ruthenium species. The latter was believed to be unstable and to undergo oxidative addition of an ortho phenyl C-H bond to form the product {Figure 3-1}. The reaction with phenyllithium was presumed to follow a similar route.[97] There is an analogy with the reaction of trans-$PtHCl(PPh_3)_2$ with methylmagnesium bromide.[2] The initially formed product,

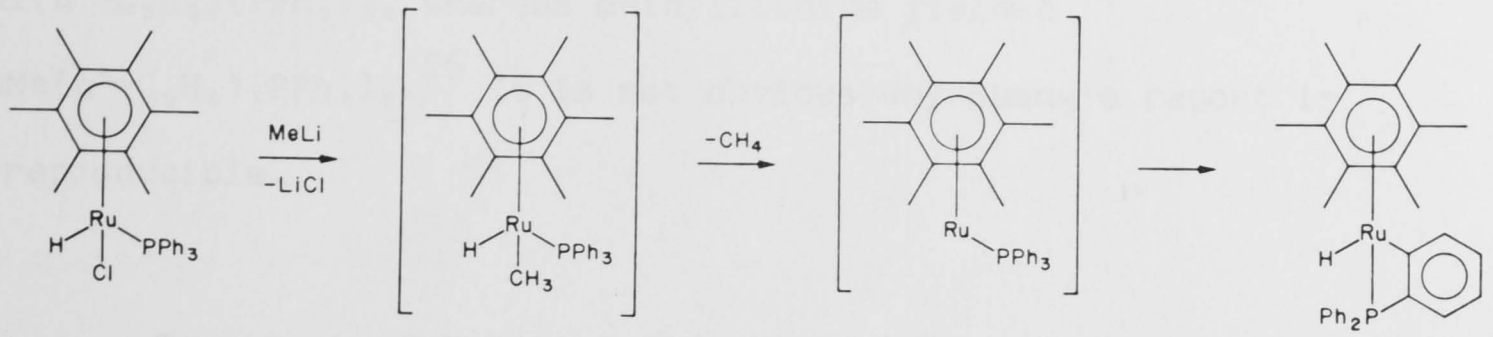


Figure 3-1: Reaction path for cyclometallation of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$.

cis-$PtH(CH_3)(PPh_3)_2$, which was spectroscopically characterized, subsequently eliminated methane to give the unsaturated zero-valent metal fragment $Pt(PPh_3)_2$. The latter disproportionated to platinum metal and $Pt(PPh_3)_3$, or was trapped with other ligands to yield $Pt(PPh_3)_2L$.

This chapter is concerned with the treatment of the hydrido complexes $RuHCl(\eta^6\text{-}C_6Me_6)L$ with various alkylating agents, and the characterization of the products of these reactions.

RESULTS

1) L = PPh_3

Attempts to repeat the synthesis of $Ru\overline{H(o\text{-}C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$ [27] by treatment of $RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_3)$ with EtMgBr, even when present in large excess, were not successful, and only resulted in partial halide metathesis of the starting material. The failure to undergo further reaction may be due in part to the inertness of ruthenium-bromine bonds relative to ruthenium-chlorine bonds. Similar results have been reported for the reaction of $RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2$ with various alkylating agents; methylmagnesium iodide gave only

$RuI(\eta^5\text{-}C_5H_5)(PPh_3)_2$, whereas methyllithium yielded $RuMe(\eta^5\text{-}C_5H_5)(PPh_3)_2$.[26] It is not obvious why Huang's report is irreproducible.

Treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ with methyllithium or phenyllithium did form the cyclometallated product $\overline{RuH(\underline{o}\text{-}C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$ [27] in 58% and 55% isolated yields, respectively. The ^1H NMR spectrum of [27] showed a doublet resonance at δ -7.58ppm ($^2J_{PH}$ = 41.0Hz) and a singlet at δ 1.95ppm due to the hexamethylbenzene protons. There was also a series of multiplets due to the aryl protons between δ 6.7 and 8.1ppm. The $^{31}P[^1H]$ NMR spectrum of [27] displayed a singlet at δ -8.4ppm, which was over 60ppm upfield from the chemical shift of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$, consistent with the presence of a four-membered ring containing phosphorus.[67] The infrared spectrum of [27] {Figure 3-2} showed a broad, medium intensity peak at 1940cm^{-1} due to ν(RuH), and sharp bands at 1555, 1413 and 720cm^{-1} characteristic of <u>ortho</u>-metallation.[20,50,133] The spectroscopic data observed for [27] agree well with those reported by Huang.[97]

However, when the crude reaction mixture formed by treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ with phenyllithium was studied by ^1H and $^{31}P[^1H]$ NMR spectroscopy, a small quantity of $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PPh_3)$ [28] {about 6%} was detected, in addition to [27]. The hydride resonance due to [28] was a doublet at δ -10.34ppm ($^2J_{PH}$ = 55.0Hz), and the signal due to the hexamethylbenzene protons was a singlet at δ 1.67ppm. The ^{31}P resonance of [28] occurred at δ 60.0ppm. The assignment of these NMR data was based on comparison with the spectroscopic properties of other hydridophenyl compounds prepared during this work {see below}. A small quantity of what is believed to be the compound $\overline{RuBr(\underline{o}\text{-}C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$ was also detected in the

mixture, and it was identified by its NMR parameters {$\delta(C_6(C\underline{H}_3)_6)$ = 1.74ppm, $\delta(P)$ = -24.5ppm}. This compound was also formed in the reaction of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ with EtMgBr containing excess bromoethane. The phenyllithium may have contained some unreacted bromobenzene which gave rise to the bromometallacycle.

In an attempt to verify the pathway shown in Figure 3-1, an independent route to the methyl hydride $RuH(CH_3)(\eta^6\text{-}C_6Me_6)(PPh_3)$ was sought. The known compound $Ru(CH_3)(O_2CCF_3)(\eta^6\text{-}C_6Me_6)(PPh_3)$,[180] when treated on a 90mg scale with 20mg of sodium borohydride, formed $\overline{RuH(\underline{o}\text{-}C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$ [27] in 16% yield. However, when this reaction was repeated on a preparative scale, fine red crystals were isolated. The infrared spectrum of the red crystals showed broad, medium intensity peaks at 2360, 2305 and 2285cm^{-1} as well as ν(RuH) at 1963cm^{-1}. The ^1H NMR spectrum showed a very broad resonance at δ -4.25ppm, as well as a low intensity doublet at δ -11.11ppm with a coupling of 38.5Hz {probably to phosphorus}. There were also resonances at δ 1.73 and 1.99ppm (6:1) due to hexamethylbenzene ligands, and multiplets between δ 7 and 8ppm due to triphenylphosphine. The spectroscopic data suggest that the compound was a borohydride complex such as $RuH(BH_4)(\eta^6\text{-}C_6Me_6)(PPh_3)$, but low yields hampered the characterization of this material. The filtrate appeared to contain a mixture of the unidentified red complex and [27]. Use of $LiAlH_4$ or Red-Al in place of $NaBH_4$ in the above reaction was unsuccessful; on methanolysis and evaporation of the solvent, tarry brown residues were formed.

The result of the reaction between $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ and Red-Al depended on the stoichiometry. NMR spectra of the crude reaction mixtures formed when $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ was treated with

1.4 equivalents of Red-Al at room temperature showed that only 30 to 50% of $\overline{RuH(\underline{o}\text{-}C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$ [27] and 5% of the known dihydride $RuH_2(\eta^6\text{-}C_6Me_6)(PPh_3)$[180] were formed. Heating the reaction mixture only increased the quantity of dihydride. However, conversion to [27] was rapid and quantitative when 5 equivalents of Red-Al were used. The pathway for the reaction between $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ and Red-Al is not clear. The suggestion that $RuH_2(\eta^6\text{-}C_6Me_6)(PPh_3)$ is formed and subsequently eliminates H_2[97] is clearly incorrect in the light of the thermal stability of the dihydride.[180] However, Red-Al may be acting as a strong base. It was found that when $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ was heated with sodium hydroxide in 2-propanol, the main product was the cyclometallated complex [27], but the dihydride and other unidentified species were also present. Treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ with the strong, non-nucleophilic bases DBN, DBU, $KOBu^t$, and $NaN(SiMe_3)_2$ in toluene gave little or no reaction. Prolonged heating of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ with $KOBu^t$ or $NaN(SiMe_3)_2$ led to decomposition.

Although the following results do not strictly belong in this section, this is the most appropriate place to discuss them. The hydrides $RuHCl(\eta^6\text{-}C_6Me_6)(PMePh_2)$ and $RuHCl(\eta^6\text{-}C_6Me_6)(PPr^i_3)$ behaved quite differently from $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ on treatment with a large excess of Red-Al. The dihydride $RuH_2(\eta^6\text{-}C_6Me_6)(PMePh_2)$ was the chief product from $RuHCl(\eta^6\text{-}C_6Me_6)(PMePh_2)$, although a small quantity of the ortho-metallated species {see below} was also detected. There was little reaction between $RuHCl(\eta^6\text{-}C_6Me_6)(PPr^i_3)$ and excess Red-Al over a period of 80min, although a small quantity of cyclometallated species {see below} and possibly some dihydride were formed. In these cases, therefore, Red-Al does not behave as a base. If Red-Al were able to act in this way, deprotonation of the relatively acidic methyl group of $PMePh_2$ and subsequent cyclometallation to form a $\overline{RuCH_2PPh_2}$

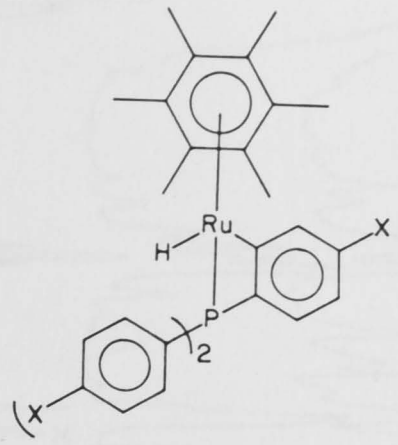
containing species might have been expected, but this was not observed. The lack of reactivity of Red-Al towards $RuHCl(\eta^6\text{-}C_6Me_6)(PPr^i_3)$ may be due to steric hindrance by the bulky phosphine to the reagent.

A number of methylating agents were studied as possible alternatives to methyllithium in the reaction with $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$. Treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ with trimethylaluminium at room temperature caused slight gas evolution, the reaction mixture paled significantly and a white precipitate formed. However, on work-up, the crude reaction mixture was found to contain largely unchanged starting material. Similar treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ with lithium dimethylcuprate led to extensive decomposition. The isolated solid was a mixture containing a large number of compounds, the main organometallic component being $RuMe_2(\eta^6\text{-}C_6Me_6)(PPh_3)$.[180] The reaction between $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ and dimethylzinc did not go to completion, and again a mixture was formed.

Treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(EPh_3)$ {E = As, Sb} with methyllithium led to decomposition. The reason for this is not known, because Huang[97] reported the synthesis of $\overline{RuH(\underline{o}\text{-}C_6H_4EPh_2)}(\eta^6\text{-}C_6Me_6)$ from $RuCl_2(\eta^6\text{-}C_6Me_6)(EPh_3)$ {E = As, Sb} and EtMgBr. This suggests that the observed decomposition was not due to inherent instability of the cyclometallated complexes. However, the weakly bound arsine or stibine ligand may be displaced during the reaction, possibly by the excess of methyllithium used.

2) $L = P(p\text{-}C_6H_4X)_3$

The reaction between the hydrides $RuHCl(\eta^6\text{-}C_6Me_6)(P[\underline{p}\text{-}C_6H_4X]_3)$ {X = F, CH_3} and methyllithium proceeded similarly to that of



[29] {X = F}; [30] {X = CH_3}

the triphenylphosphine complex. The spectroscopic data for the products, $\overline{RuH([\underline{o}\text{-}C_6H_3\text{-}\underline{p}\text{-}X]P[\underline{p}\text{-}C_6H_4X]_2)}(\eta^6\text{-}C_6Me_6)$, were almost identical with those previously reported.[97] The ^{19}F NMR spectrum of [29] {X = F} consisted of three different fluorine resonances, as expected for a chiral complex with diastereotopic aryl rings. The ^1H NMR spectrum of [30] {X = CH_3} showed distinct methyl resonances for the metallated and unmetallated rings respectively {see Table 3-1}. The <u>p</u>-tolyl compound [30] showed characteristic bands for <u>ortho</u>-metallation in the infrared spectrum at 1555, 1410 and 730cm^{-1}. The corresponding bands in the spectrum of the <u>p</u>-fluorophenyl complex [29] were obscured by other bands due to the ligand.

<u>3) L = PBu^tPh_2</u>

The reaction between $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tPh_2)$ and methyllithium at room temperature gave a mixture of two products. When the mixture was heated, one component disappeared. When the reaction was carried out at 0°, a white powder was isolated in 55% yield. The analytical and spectroscopic data {Tables 3-1 to 3-3, 3-6} were consistent with the product being one compound, $\overline{RuH(CH_2CMe_2PPh_2)}(\eta^6\text{-}C_6Me_6)$ [31], in which a <u>t</u>-butyl methyl group is metallated.

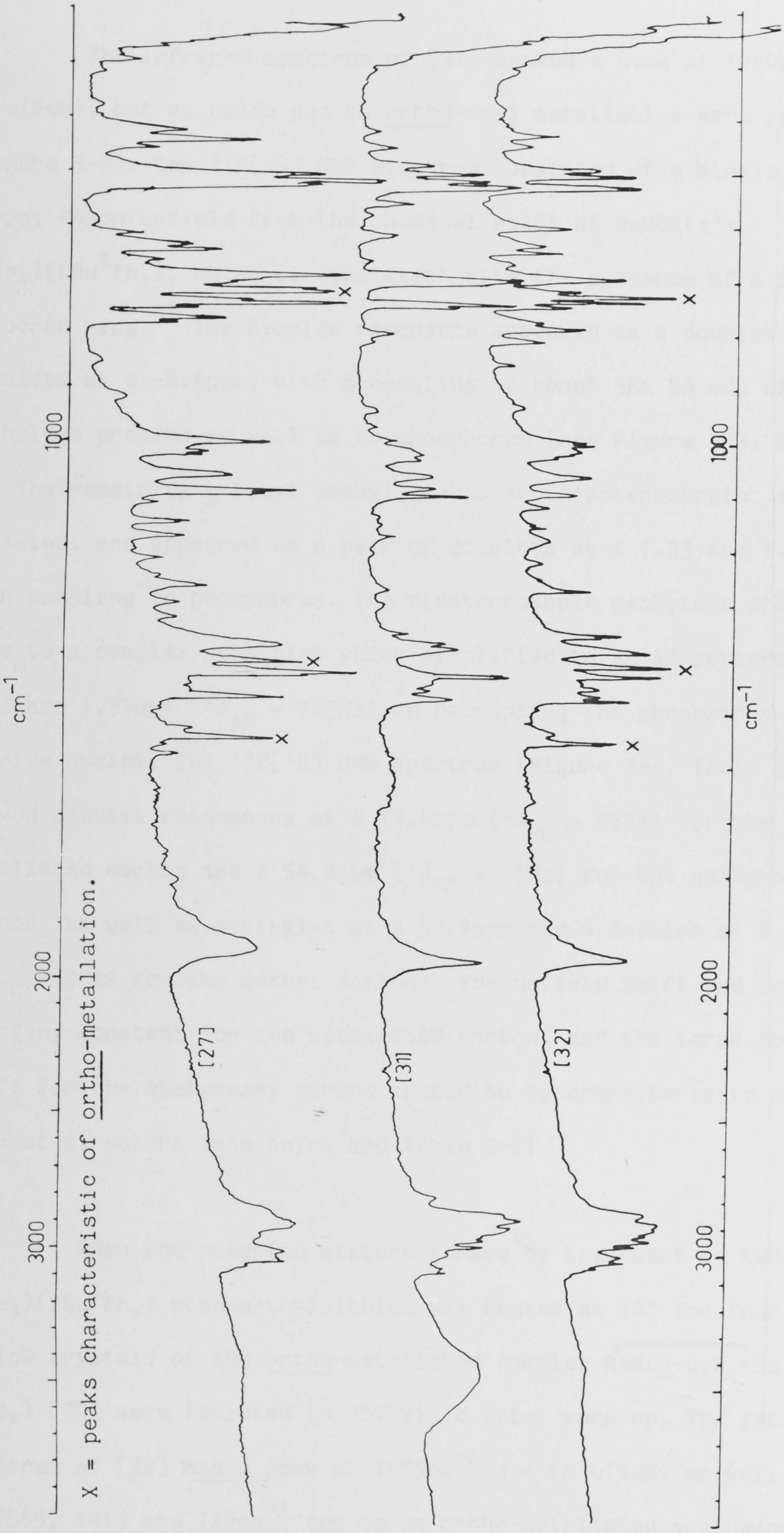


Figure 3-2: Infrared spectra of $\overline{RuH(\underline{o}\text{-}C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$ [27], $\overline{RuH(CH_2CMe_2PPh_2)}(\eta^6\text{-}C_6Me_6)$ [31] and $\overline{RuH(\underline{o}\text{-}C_6H_4PBu^tPh)}(\eta^6\text{-}C_6Me_6)$ [32].

The infrared spectrum of [31] showed a peak at 1960cm^{-1} due to ν(RuH), but no bands due to ortho-aryl metallation were present {Figure 3-2}. The $^{31}P[^{1}H]$ NMR spectrum consisted of a single peak at δ 26ppm, 44ppm upfield from the chemical shift of $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tPh_2)$, which is consistent with the presence of a four-membered ring.[67] The hydride resonance appeared as a doublet of doublets at δ -8.8ppm, with a coupling of about 3Hz to one of the methylene protons as well as to phosphorus {see Figure 3-3, Table 3-1}. The remaining t-butyl methyl groups are diastereotopic, as expected, and appeared as a pair of doublets at δ 1.33 and 1.35ppm, with coupling to phosphorus. The diastereotopic methylene protons gave rise to a complex multiplet which simplified to an AB pattern at δ 1.02 and 1.39ppm ($^2J_{AB}$ = 7.3Hz) on decoupling the phosphorus and hydride nuclei. The $^{13}C[^{1}H]$ NMR spectrum {Figure 3-4, Table 3-2} showed doublet resonances at δ 11.4ppm ($^2J_{PC}$ = 43Hz) for the metallated carbon and δ 54.6ppm ($^1J_{PC}$ = 35Hz) for the quaternary carbon, as well as a singlet at δ 30.7ppm and a doublet at δ 30.9ppm ($^2J_{PC}$ = 3Hz) for the methyl carbons. The upfield shift and large coupling constant for the metallated carbon, and the large downfield shift for the quaternary carbon appear to be characteristic of this type of structure {see below and Table 3-2}.

When the reaction mixture formed by treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tPh_2)$ with methyllithium was heated at 70° for four hours, yellow crystals of the ortho-metallated complex $\overline{RuH(o\text{-}C_6H_4}PBu^tPh)(\eta^6\text{-}C_6Me_6)$ [32] were isolated in 40% yield after work-up. The infrared spectrum of [32] had a peak at 1955cm^{-1} due to ν(RuH) as well as bands at 1555, 1413 and 728cm^{-1} due to an ortho-metallated aryl group {Figure 3-2}. The $^{13}C[^{1}H]$ NMR {Figure 3-4} and ^{1}H NMR spectra of [32] showed a single doublet arising from the t-butyl group; the quaternary

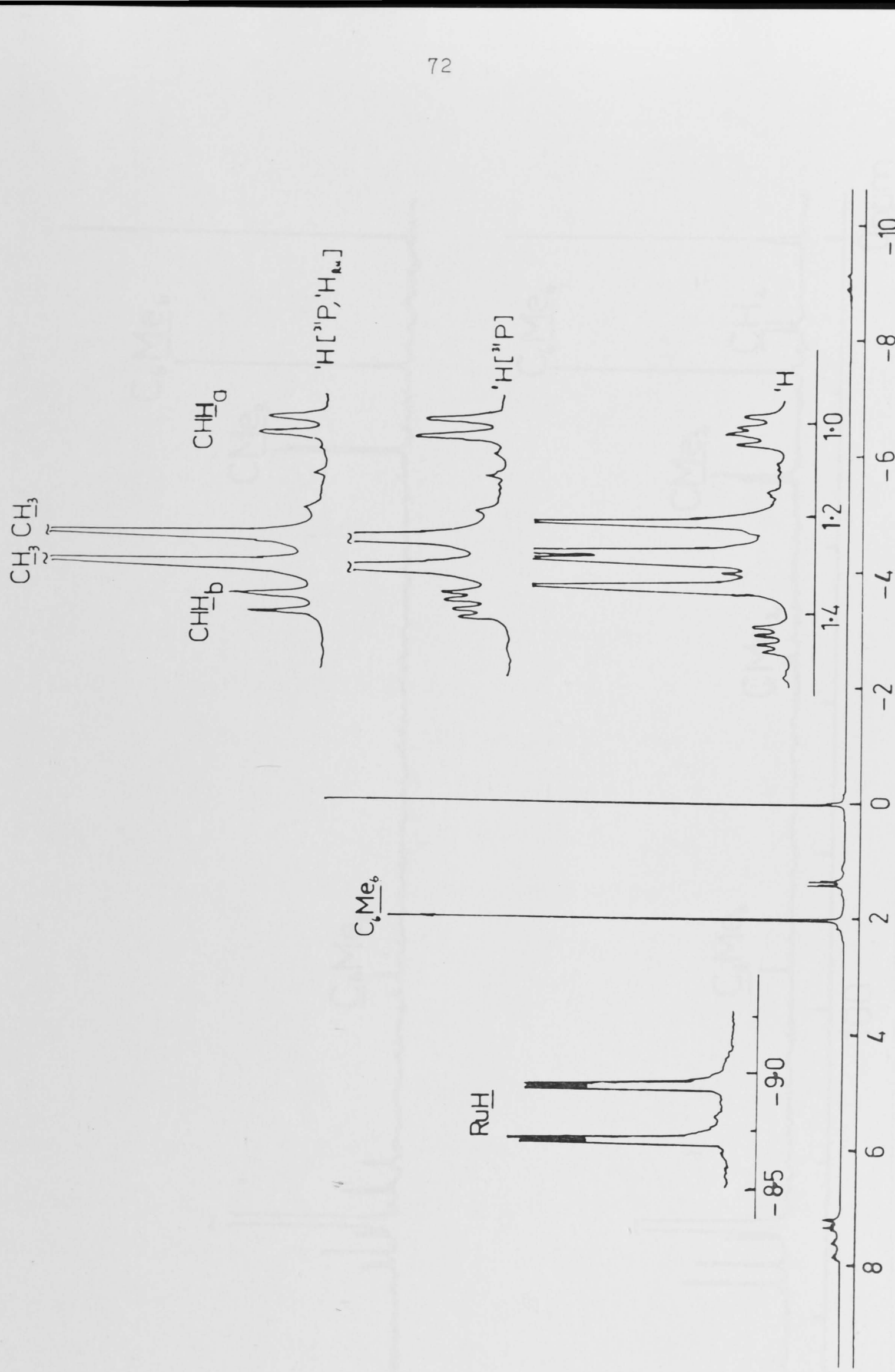


Figure 3-3: ^1H NMR spectrum of $\overline{RuH(CH_2CMe_2PPh_2)}(\eta^6\text{-}C_6Me_6)$ [31].

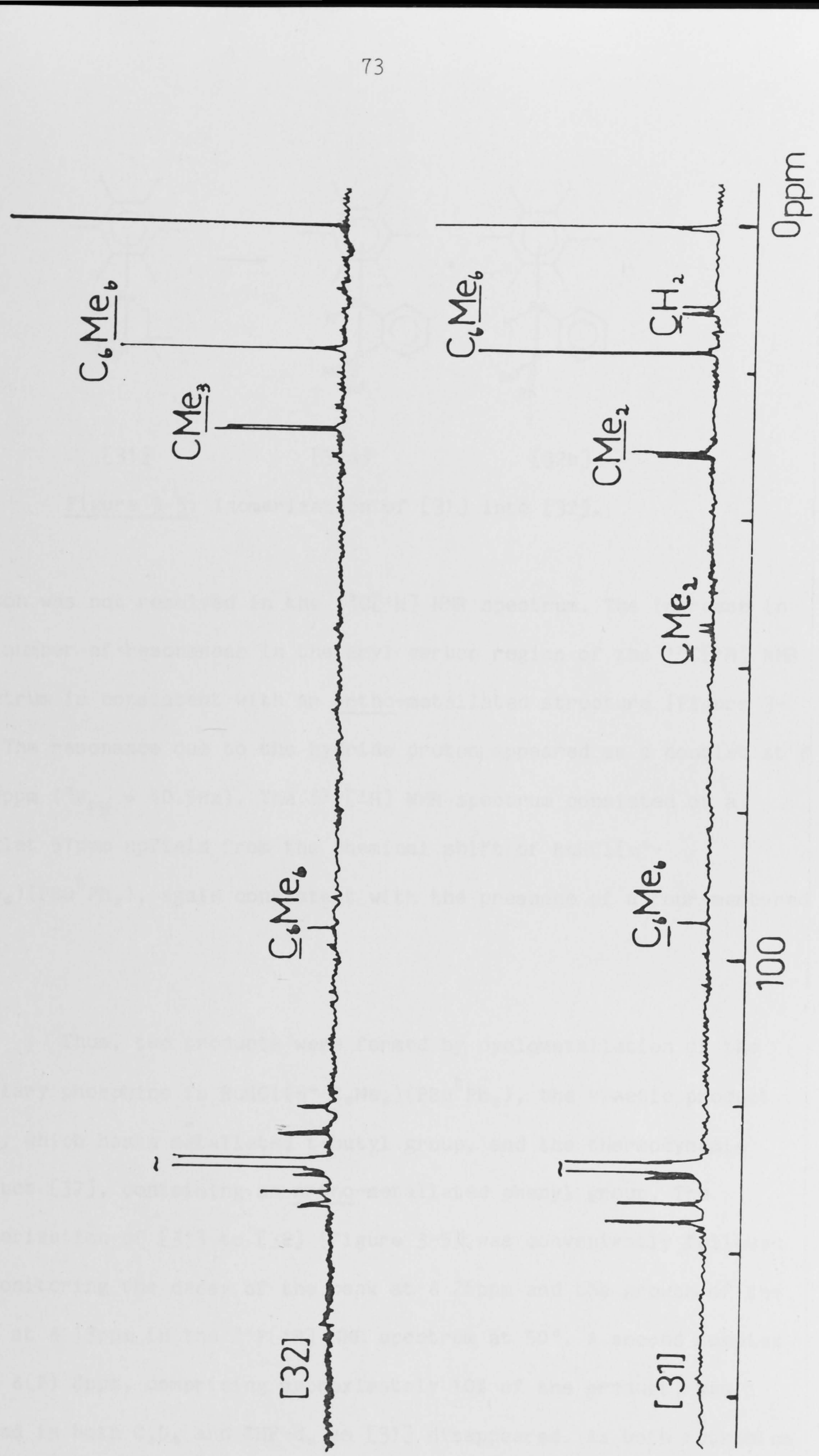
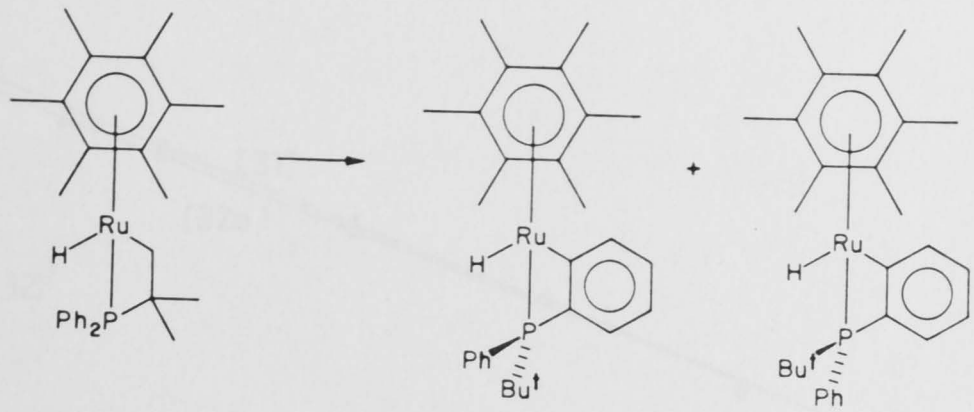


Figure 3-4: $^{13}C[^{1}H]$ NMR spectrum of $\overline{RuH(CH_2CMe_2PPh_2)}(\eta^6\text{-}C_6Me_6)$ [31] and $\overline{RuH(\underline{o}\text{-}C_6H_4PBu^tPh)}(\eta^6\text{-}C_6Me_6)$ [32].

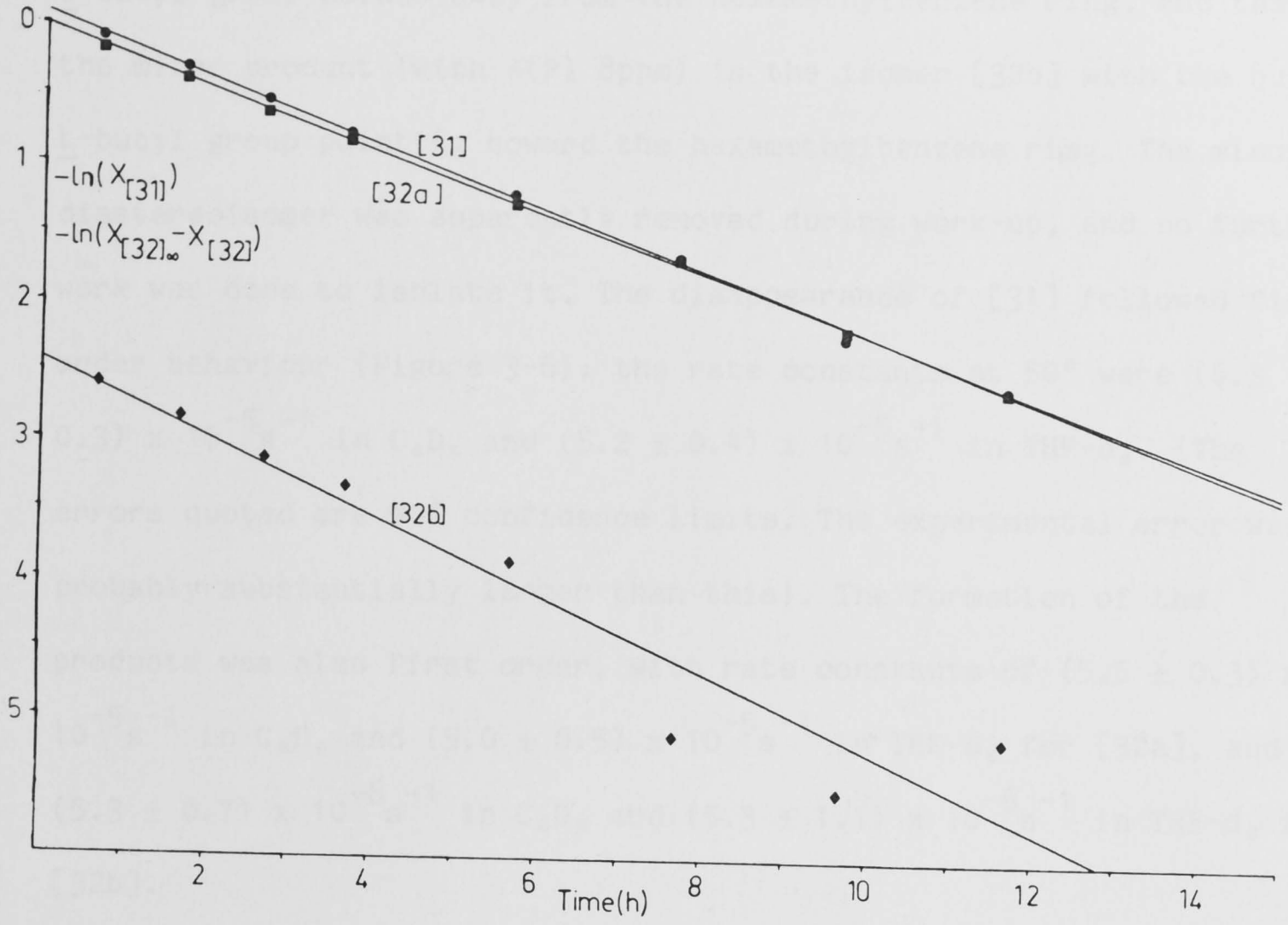


[31] [32a] [32b]

Figure 3-5: Isomerization of [31] into [32].

carbon was not resolved in the $^{13}C[^1H]$ NMR spectrum. The increase in the number of resonances in the aryl carbon region of the $^{13}C[^1H]$ NMR spectrum is consistent with an ortho-metallated structure {Figure 3-4}. The resonance due to the hydride proton appeared as a doublet at δ -8.0ppm ($^2J_{PH}$ = 40.5Hz). The $^{31}P[^1H]$ NMR spectrum consisted of a singlet 57ppm upfield from the chemical shift of $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tPh_2)$, again consistent with the presence of a four-membered ring.

Thus, two products were formed by cyclometallation of the tertiary phosphine in $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tPh_2)$, the kinetic product [31], which has a metallated t-butyl group, and the thermodynamic product [32], containing an ortho-metallated phenyl group. The isomerization of [31] to [32] {Figure 3-5} was conveniently followed by monitoring the decay of the peak at δ 26ppm and the growth of the peak at δ 13ppm in the $^{31}P[^1H]$ NMR spectrum at 50°. A second complex with δ(P) 8ppm, comprising approximately 10% of the product, was formed in both C_6D_6 and THF-d_8 as [31] disappeared. As both ruthenium and phosphorus were chiral centres in [32], a pair of diastereoisomers [32a] and [32b] could exist {Figure 3-5}. It is suggested that the isolated product was the diastereoisomer [32a], in which the bulky



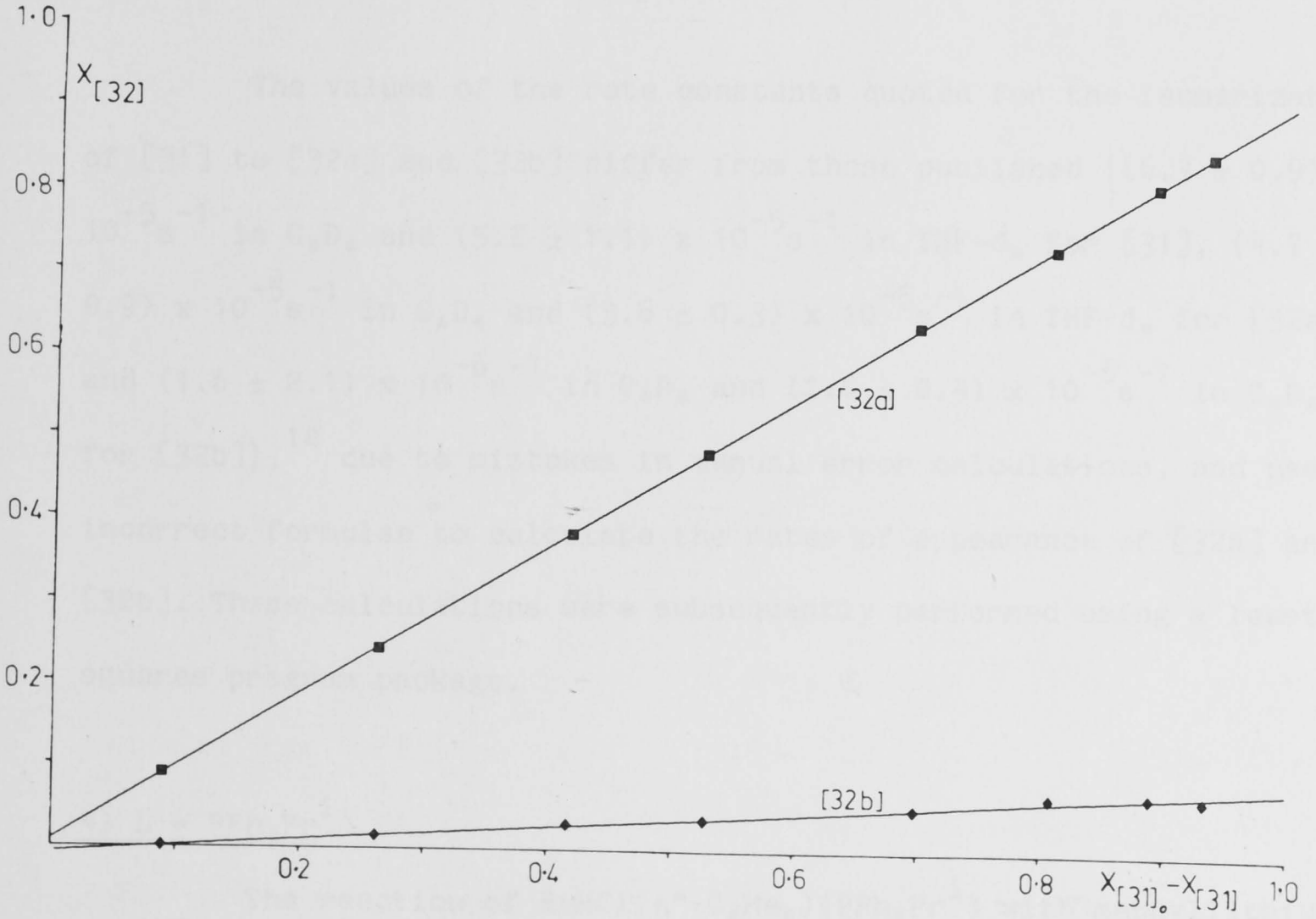


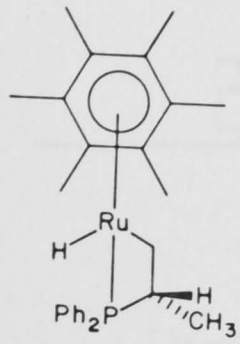
Figure 3-6: Plot of data for the isomerization of $\overline{RuH(CH_2CMe_2PPh_2)}(\eta^6$-$C_6Me_6)$ [31] to $\overline{RuH(\underline{o}\text{-}C_6H_4PBu^tPh)}(\eta^6\text{-}C_6Me_6)$ [32] in C_6D_6, including lines of best fit. For explanation of symbols, see appendix 2, p188.

t-butyl group points away from the hexamethylbenzene ring, and that the minor product {with δ(P) 8ppm} is the isomer [32b] with the bulky t-butyl group pointing toward the hexamethylbenzene ring. The minor diastereoisomer was apparently removed during work-up, and no further work was done to isolate it. The disappearance of [31] followed first-order behaviour {Figure 3-6}; the rate constants at 50° were (6.3 ± 0.3) x $10^{-5}s^{-1}$ in C_6D_6 and (5.2 ± 0.4) x $10^{-5}s^{-1}$ in THF-d_8. {The errors quoted are 90% confidence limits. The experimental error was probably substantially larger than this}. The formation of the products was also first order, with rate constants of (5.5 ± 0.3) x $10^{-5}s^{-1}$ in C_6D_6 and (5.0 ± 0.5) x $10^{-5}s^{-1}$ in THF-d_8 for [32a], and (5.3 ± 0.7) x $10^{-6}s^{-1}$ in C_6D_6 and (5.3 ± 1.1) x $10^{-6}s^{-1}$ in THF-d_8 for [32b].

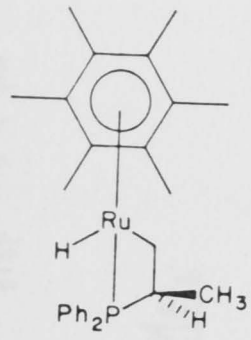
The values of the rate constants quoted for the isomerization of [31] to [32a] and [32b] differ from those published {(6.3 ± 0.9) x $10^{-5}s^{-1}$ in C_6D_6 and (5.2 ± 1.1) x $10^{-5}s^{-1}$ in THF-d_8 for [31], (4.7 ± 0.9) x $10^{-5}s^{-1}$ in C_6D_6 and (3.6 ± 0.3) x $10^{-5}s^{-1}$ in THF-d_8 for [32a], and (1.6 ± 2.1) x $10^{-6}s^{-1}$ in C_6D_6 and (1.8 ± 0.4) x $10^{-6}s^{-1}$ in C_6D_6 for [32b]},[14] due to mistakes in manual error calculations, and use of incorrect formulae to calculate the rates of appearance of [32a] and [32b]. These calculations were subsequently performed using a least-squares program package.

4) L = PPh_2Pr^i

The reaction of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2Pr^i)$ with methyllithium, even at -12°, gave a solution which showed three hydride resonances in its ^{1}H NMR spectrum, a doublet at δ -8.03ppm ($^2J_{PH}$ = 41.5Hz), an approximate doublet of triplets at δ - 8.17ppm ($^2J_{PH}$ = 45Hz, further couplings not resolved) and a doublet of doublets at δ -8.90ppm ($^2J_{PH}$



[33a]



[33b]

= 49Hz, $^{3}J_{HH}$ ca. 2Hz). On heating the sample in toluene at 60° for four hours, the latter two resonances disappeared, and were thus assigned to the diastereoisomers of the isopropyl metallated product [33a] and [33b], in which the ruthenium and methine carbons were the chiral centres. The remaining hydride resonance was assigned to the ortho-metallated product [34]. Treatment of $RuHCl(\eta^{6}\text{-}C_{6}Me_{6})(PPh_{2}Pr^{i})$ with methyllithium at -18°, and careful workup at low temperature gave a pale yellow solid, which, according to ^{1}H NMR spectroscopy, was a mixture consisting mainly of [33a] and [33b] in the ratio 1.6:1, but which also contained approximately 13% [34]. It is suggested that the major diastereoisomer has the metallacyclic methyl group pointing away from the hexamethylbenzene ring.

The infrared spectrum of the mixture obtained as described above {Table 3-3} showed a band at 1910cm^{-1} due to ν(RuH). No bands characteristic of ortho-metallation were observed. The ^{1}H NMR spectrum was very complex in the region δ 0.7 to 1.7 and 3.3 to 4.3ppm. There were resonances at δ 1.93 and 2.01ppm due to the hexamethylbenzene protons of [33a] and [33b], as well as at δ 2.12ppm due to the hexamethylbenzene protons of [34]. The appearance of the hydride region was as described above. The $^{31}P[^{1}H]$ NMR spectrum consisted of singlets at δ 9.0 and 12.5ppm due to [33a] and [33b] as well as minor

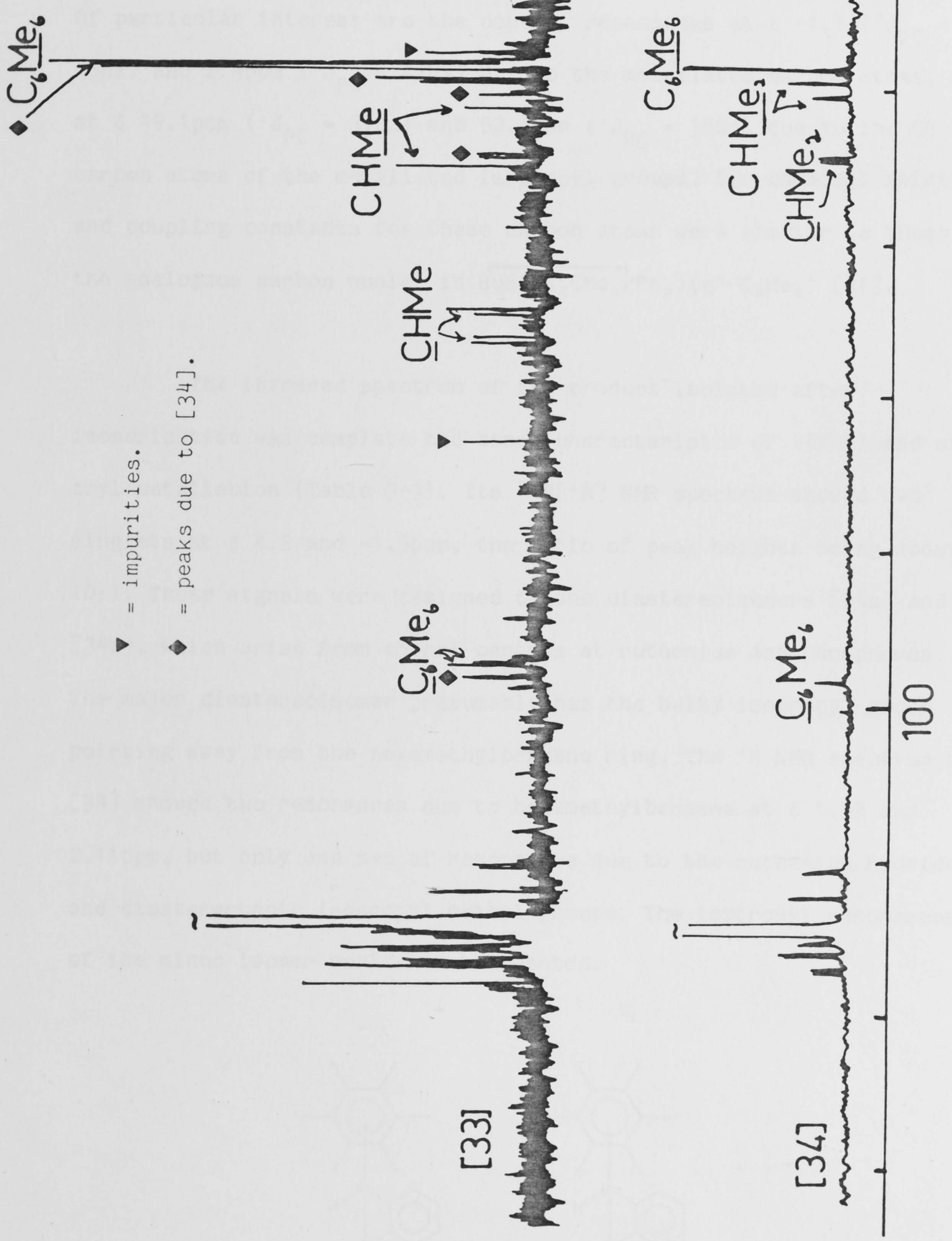
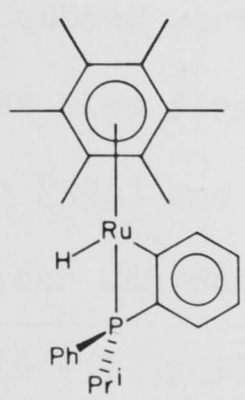


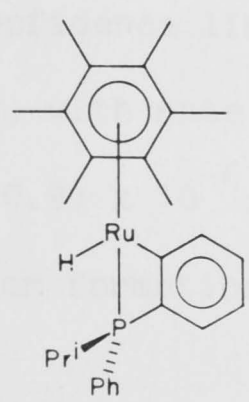
Figure 3-7: $^{13}C[^{1}H]$ NMR spectra of $\overline{RuH(CH_2CHMePPh_2)}(\eta^6\text{-}C_6Me_6)$ [33] and $\overline{RuH(\underline{o}\text{-}C_6H_4PPhPr^i)}(\eta^6\text{-}C_6Me_6)$ [34].

singlets at δ 4.2 and -1.9ppm due to [34]. The $^{13}C[^1H]$ NMR spectrum of the mixture {Figure 3-7} was complex, but a complete assignment was possible {Table 3-2} and was consistent with the proposed structures. Of particular interest are the doublet resonances at δ -1.1 ($^2J_{PC}$ = 45Hz) and 2.4ppm ($^2J_{PC}$ = 42Hz) due to the metallated carbon atoms, and at δ 49.1ppm ($^1J_{PC}$ = 37Hz) and 52.7ppm ($^1J_{PC}$ = 38Hz) due to the CH carbon atoms of the metallated isopropyl groups. The chemical shifts and coupling constants for these carbon atoms were similar to those of the analogous carbon nuclei in $\overline{RuH(CH_2CMe_2PPh_2)}(\eta^6\text{-}C_6Me_6)$ [31].

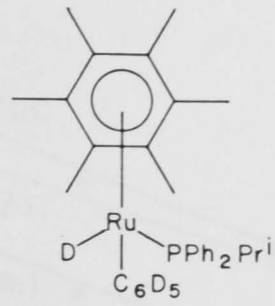
The infrared spectrum of the product isolated after isomerization was complete had bands characteristic of ν(RuH) and of aryl metallation {Table 3-3}. Its $^{31}P[^1H]$ NMR spectrum showed two singlets at δ 4.2 and -1.9ppm, the ratio of peak heights being about 10:1. These signals were assigned to the diastereoisomers [34a] and [34b], which arise from chiral centres at ruthenium and phosphorus. The major diastereoisomer presumably has the bulky isopropyl group pointing away from the hexamethylbenzene ring. The ^1H NMR spectrum of [34] showed two resonances due to hexamethylbenzene at δ 1.93 and 2.11ppm, but only one set of resonances due to the ruthenium hydride and diastereotopic isopropyl methyl groups. The isopropyl resonances of the minor isomer could not be located.



[34a]

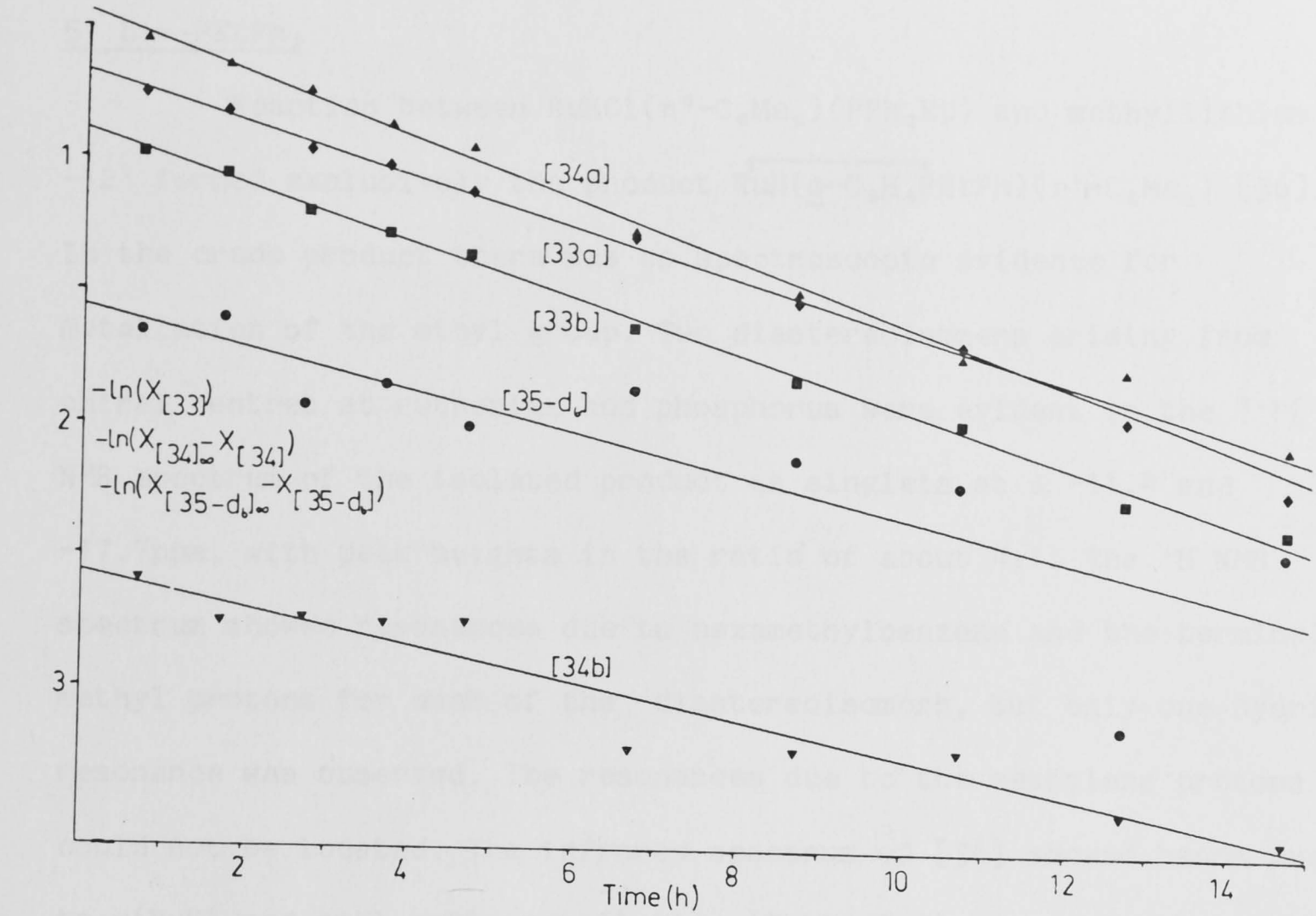


[34b]



[35-d_6]

The isomerization of [33] to [34] in C_6D_6 at 20° was conveniently monitored by $^{31}P[^1H]$ NMR spectroscopy. An unexpected by-product was formed during the isomerization. The resonance due to this species was outside the sweep width of the spectra recorded to monitor the isomerization kinetics, but was observed in a subsequent spectrum. The resonance for the by-product occurred at δ 67.8ppm in the $^{31}P[^1H]$ NMR spectrum as a 1:1:1 triplet with a coupling of 7Hz. This was probably due to the species $RuD(C_6D_5)(\eta^6\text{-}C_6Me_6)(PPh_2Pr^i)$ [35-d_6] formed by attack of the fragment $Ru(\eta^6\text{-}C_6Me_6)(PPh_2Pr^i)$ on a C-D bond of C_6D_6. The rate of formation of [35-d_6] was measured by monitoring the drop in intensity of [33] + [34] relative to Ph_3PO which had been added as an internal standard, so the data for [35-d_6] were not very reliable. The isomerization of [33a] and [33b] were first order {Figure 3-8}, and the rate constants were equal within experimental error, being $(2.9 \pm 0.2) \times 10^{-5} s^{-1}$ for [33a] and $(2.6 \pm 0.2) \times 10^{-5} s^{-1}$ for [33b] {errors quoted were 90% confidence limits}. Formation of [34a] and [34b] was also first order, with rate constants of $(2.4 \pm 0.6) \times 10^{-5} s^{-1}$ for [34a] and $(2.3 \pm 0.9) \times 10^{-6} s^{-1}$ for [34b]. Pseudo-first order behaviour was observed for formation of [35-d_6], with a rate constant of $(6 \pm 3) \times 10^{-6} s^{-1}$.



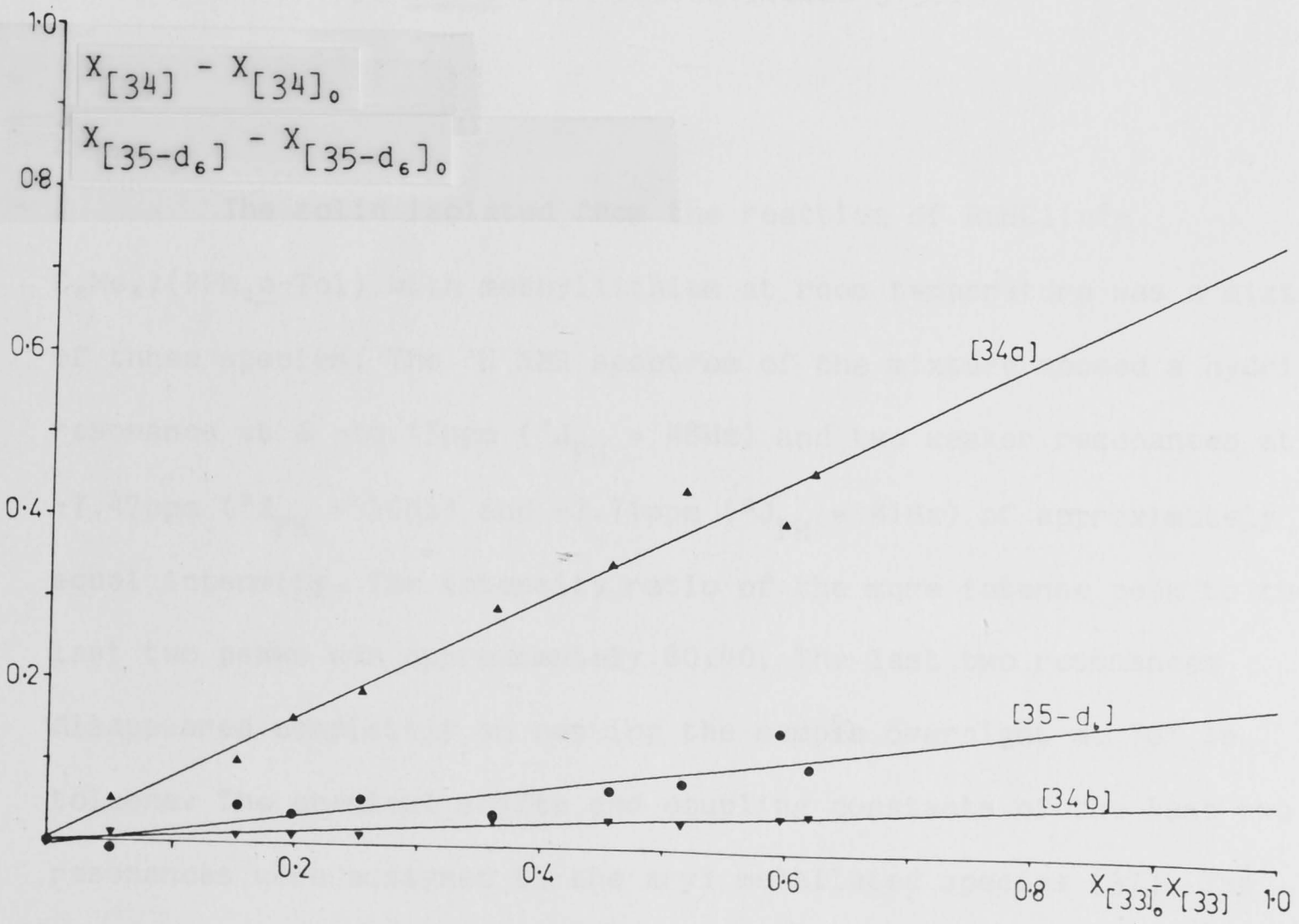


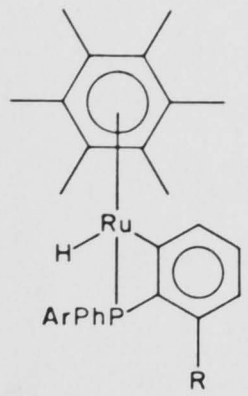
Figure 3-8: Plot of data for isomerization of $\overline{RuH(CH_2CHMePPh_2)}(\eta^6\text{-}C_6Me_6)$ [33] into $\overline{RuH(\underline{o}\text{-}C_6H_4PPhPr^i)}(\eta^6\text{-}C_6Me_6)$ [34] plus formation of $RuD(C_6D_5)(\eta^6\text{-}C_6Me_6)(PPh_2Pr^i)$ [35-d_6] in C_6D_6, including lines of best fit. For explanation of symbols, see appendix 2, p188.

5) L = $PEtPh_2$

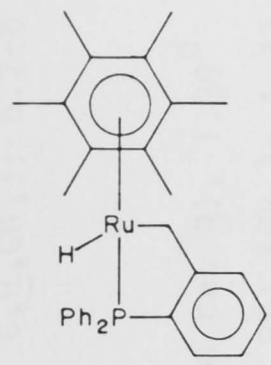
Reaction between $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2Et)$ and methyllithium at -12° formed exclusively the product $\overline{RuH(\underline{o}\text{-}C_6H_4PEtPh)}(\eta^6\text{-}C_6Me_6)$ [36]. In the crude product there was no spectroscopic evidence for metallation of the ethyl group. Two diastereoisomers arising from chiral centres at ruthenium and phosphorus were evident in the $^{31}P[^1H]$ NMR spectrum of the isolated product as singlets at δ -11.4 and -17.7ppm, with peak heights in the ratio of about 4:1. The ^1H NMR spectrum showed resonances due to hexamethylbenzene and the terminal methyl protons for each of the diastereoisomers, but only one hydride resonance was observed. The resonances due to the methylene protons could not be located. The infrared spectrum of [36] showed bands due to ν(RuH) and aryl ortho-metallation {Table 3-3}.

6) L = PPh_2o-Tol

The solid isolated from the reaction of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2\underline{o}\text{-Tol})$ with methyllithium at room temperature was a mixture of three species. The ^1H NMR spectrum of the mixture showed a hydride resonance at δ -10.15ppm ($^2J_{PH}$ = 48Hz) and two weaker resonances at δ -7.47ppm ($^2J_{PH}$ = 40Hz) and -7.71ppm ($^2J_{PH}$ = 41Hz) of approximately equal intensity. The intensity ratio of the more intense peak to the last two peaks was approximately 60:40. The last two resonances disappeared completely on heating the sample overnight at 70° in toluene. The chemical shifts and coupling constants of the last two resonances were assigned to the aryl metallated species [37]. The $^{31}P[^1H]$ NMR spectrum of the mixture showed two singlets, at δ -10.6 and 69.4ppm, of which the former disappeared on heating. The chemical shift of the former, due to [37], was shifted 64ppm upfield from that of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2\underline{o}\text{-Tol})$, whilst the latter resonance, due to [38], was 17ppm downfield, which suggests that they arise from



[37]



[38]

{R=H, Ar=o-Tol; R=Me, Ar=Ph}

compounds containing four and five-membered rings, respectively.[67]

The yellow crystalline solid isolated after the mixture had been heated in toluene at 70° for 14h was [38], formed by metallation of the ortho-methyl group. There were barely detectable traces of the isomers of [37] present in the sample. The infrared spectrum of [38] showed no bands due to ortho-aryl metallation. The ^{1}H NMR spectrum of [38] displayed the methylene protons as an AB pattern at δ ca. 3ppm. Treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2o\text{-}Tol)$ with methyllithium at -10° gave mainly [38] and the isomer of [37] giving rise to the hydride resonance at δ -7.47ppm, but very little of the isomer of [37] giving rise to the hydride resonance at δ -7.71ppm was formed. Thus metallation of the tolyl methyl group competes with, and is thermodynamically favoured over, aryl metallation. The thermodynamic product [38] was independently synthesized by heating the chloro complex $RuCl(o\text{-}CH_2C_6H_4PPh_2)(\eta^6\text{-}C_6Me_6)$ [26] {see Chapter 2} with sodium borohydride in 2-propanol for forty hours. The product was spectroscopically identical with the product obtained from $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2o\text{-}Tol)$.

Table 3-1 : ^{1}H and ^{31}P NMR Data for Cyclometallated and Hydridophenyl Complexes[a]
(* = Compound not isolated; only identified spectroscopically)

Compound	δ(P)	δ($C_6\underline{Me}_6$)	δ(Ru$\underline{H}$) ($^{2}J_{PH}$)	Other
[27] $\overline{RuH(\underline{o}\text{-}C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$	-8.4	1.95	-7.58(41.0)	6.7-8.1 (m, $C_6\underline{H}_4$ and $C_6\underline{H}_5$)
[28] $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PPh_3)$*	60.0	1.67	-10.34(55.0)	
[29] $\overline{RuH([\underline{o}\text{-}C_6H_3\text{-}\underline{p}\text{-}F]P[\underline{p}\text{-}C_6H_4F]_2)}(\eta^6\text{-}C_6Me_6)$[b]	-6.8[c]	1.84	-7.92(40.0)	6.7-8 (m, $C_6\underline{H}_3$ and $C_6\underline{H}_4$)
[30] $\overline{RuH([\underline{o}\text{-}C_6H_3\text{-}\underline{p}\text{-}CH_3]P[\underline{p}\text{-}C_6H_4CH_3]_2)}(\eta^6\text{-}C_6Me_6)$	-8.9	2.03	-7.56(40.5)	2.04 (s, $C_6H_4C\underline{H}_3$); 2.33 (s, $C_6\underline{H}_3CH_3$); 6.7-8 (m, $C_6\underline{H}_3$ and $C_6\underline{H}_4$)
[31] $\overline{RuH(CH_2CMe_2PPh_2)}(\eta^6\text{-}C_6Me_6)$	26.3[d]	1.97	-8.82(45.7)[e]	1.02[d] (dd, $^{2}J_{H^aH^b}$ =7.3, $^{3}J_{PH^a}$ ca. 4), 1.39[d] (m, $^{3}J_{H^bH}Ru$ =3.7, $^{3}J_{PH^b}$ ca. 29) ($C\underline{H}_2$); 1.33 (d, $^{3}J_{PH}$ = 15.6), 1.35 (d, $^{3}J_{PH}$ = 14.2) ($C\underline{Me}_2$); 7.0-7.8 (m, $C_6\underline{H}_5$)
[32] $\overline{RuH(\underline{o}\text{-}C_6H_4PBu^tPh)}(\eta^6\text{-}C_6Me_6)$	13.1[d]	1.93	-7.96(40.5)	1.23 (d, $^{3}J_{PH}$ = 14.2, $C\underline{Me}_3$); 6.7-8 (m, $C_6\underline{H}_4$ and $C_6\underline{H}_5$)

Table 3-1 : ^{1}H and ^{31}P NMR Data for Cyclometallated and Hydridophenyl Complexes (Cont'd)

Compound	δ(P)	δ($C_6\underline{Me}_6$)	δ(Ru$\underline{H}$) ($^2J_{PH}$)	Other
[33] $\overline{RuH(CH_2CHMePPh_2)}(\eta^6\text{-}C_6Me_6)$[f]	12.5[d]	2.01	-8.90(48.1)[e]	0.7-1.7 (m, CH$\underline{Me}$ and C$\underline{H}_2$); 3.3-4.3 (m, C$\underline{H}$)
	9.0	1.93	-8.17(45.0)[g]	
[34] $\overline{RuH(\underline{o}\text{-}C_6H_4PPhPr^i)}(\eta^6\text{-}C_6Me_6)$[f]	4.2	1.93	-8.03(41.5)	1.16 (dd, $^3J_{PH}$ = 15.6, $^3J_{HH}$ = 7.8), 1.20 (dd, $^3J_{PH}$ = 16.6, $^3J_{HH}$ ca. 7) (CH$\underline{Me}_2$); 6.5-7.6 (m, $C_6\underline{H}_4$ and $C_6\underline{H}_5$)
	-1.9	2.11		
[35-d_6] $RuD(C_6D_5)(\eta^6\text{-}C_6Me_6)(PPh_2Pr^i)$*	67.8[h]			
[36] $\overline{RuH(\underline{o}\text{-}C_6H_4PEtPh)}(\eta^6\text{-}C_6Me_6)$[f]	-11.4	1.93	-7.93(42.5)	0.93 (dt, $^3J_{PH}$ = 17.1, $^3J_{HH}$ = 7, minor), 1.09 (dt, $^3J_{PH}$ = 16.6, $^3J_{HH}$ = 7, major) (CH$_2$C$\underline{H}_3$); 6.5-7.7 (m, $C_6\underline{H}_4$ and $C_6\underline{H}_5$)
	-17.7	2.08		
[37] $\overline{RuH(\underline{o}\text{-}C_6H_4PPh\{\underline{o}\text{-}Tol\})}(\eta^6\text{-}C_6Me_6)$*	-10.6	1.94	-7.47(40.0)	Two isomers present; sample predominantly $\overline{RuH(\underline{o}\text{-}CH_2C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$ [38]
		1.93	-7.71(41.0)	
[38] $\overline{RuH(\underline{o}\text{-}CH_2C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$	69.4	1.80	-10.15(48.3)	2.86 (apparent dt, $^2J_{AB}$ = 14.2)[g], 2.95 (d) (C$\underline{H}_2$); 6.8-8.2 (m, $C_6\underline{H}_4$ and $C_6\underline{H}_5$)

Table 3-1 : ^{1}H and ^{31}P NMR Data for Cyclometallated and Hydridophenyl Complexes (Cont'd)

Compound	δ(P)	δ($C_6\underline{Me}_6$)	δ(Ru$\underline{H}$) ($^{2}J_{PH}$)	Other
[39] $Ru\overline{H(\underline{o}\text{-}C_6H_4PPhPr^n)}(\eta^6\text{-}C_6Me_6)$[f,i]	-15.8	1.93	-7.90(42.7)	0.81 (t, $^{3}J_{HH}$ = 7.3, major) 1.12 (t, $^{3}J_{HH}$ = 6.7, minor) ($CH_2CH_2C\underline{H}_3$); 0.8-2.6 (complex m, $C\underline{H}_2C\underline{H}_2CH_3$); 6.5-8.0 (m, $C_6\underline{H}_4$ and $C_6\underline{H}_5$)
	-21.3	2.10	-7.94(43.3)	
[40] $Ru\overline{H(CH_2CH_2CH_2PPh_2)}(\eta^6\text{-}C_6Me_6)$	79.3	1.82	-11.01(45.8)	1.3-2.6 (br m, $C\underline{H}_2C\underline{H}_2C\underline{H}_2$); 6.9-7.3, 7.8-8.0 (m, $C_6\underline{H}_5$)
[41] $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PPh_2Pr^n)$*	52.5	(1.73)	-10.48(51.9)	
[42] $Ru\overline{H(CH_2CMe_2PBu^tMe)}(\eta^6\text{-}C_6Me_6)$	21.3	2.05	-8.94(46.4)[e]	0.30 (br dd, $^{2}J_{H^a H^m}$ = 7.4, $^{3}J_{PH^a}$ = 6.4), 1.26 (ddd, $^{3}J_{H^m H}Ru$ = 3.5, $^{3}J_{PH^m}$ = 24.5) ($C\underline{H}_2$); 0.99 (d, $^{3}J_{PH}$ = 12.7, $C\underline{Me}_3$); 1.10 (d, $^{3}J_{PH}$ = 13.2), 1.56 (d, $^{3}J_{PH}$ = 13.7) ($C\underline{Me}_2$); 1.14 (d, $^{2}J_{PH}$ = 7.8, $P\underline{Me}$)

Table 3-1 : ^{1}H and ^{31}P NMR Data for Cyclometallated and Hydridophenyl Complexes (Cont'd)

Compound	δ(P)	δ($C_6\underline{Me}_6$)	δ(Ru$\underline{H}$) ($^{2}J_{PH}$)	Other
[43] $\overline{RuH(CH_2CMe_2}PBu^tEt)(\eta^6\text{-}C_6Me_6)$[f,j]	40.3	2.07	-9.42(46.4)[e]	0.38 (dd, $^{2}J_{H^a}{}_{H^m}$ = 7.5, $^{3}J_{PH^a}$ = 5.4, Ru$C\underline{H}_2$); 1.11 (d, $^{3}J_{PH}$ = 4.7), 1.58 (d, $^{3}J_{PH}$ =12.7) ($C\underline{Me}_2$); 1.05 (d, $^{3}J_{PH}$ = 12.2, $C\underline{Me}_3$); 1.18 (t, $^{3}J_{HH}$ = 7.7, $CH_2C\underline{H}_3$); 1.5 (superimposed P,CH_3 coupled multiplets, $C\underline{H}_2CH_3$); {1.78,(m,$^{3}J_{PH^a}$ = 11.3,Ru$CH_{a-b}\underline{H}$?)}
	48.5	2.06	-10.17(47.6)[g]	
[44] $\overline{RuH(CH_2CH_2}PBu^t_2)(\eta^6\text{-}C_6Me_6)$*	33.8[k]	(2.03)[l]	-9.52(42.7)[m]	Predominantly $\overline{RuH(CH_2CMe_2}PBu^tEt)(\eta^6\text{-}C_6Me_6)$
[45] $\overline{RuH(CH_2CMe_2}PBu^tPr^n)(\eta^6\text{-}C_6Me_6)$[f,n]	36.8	2.08	-9.45(46.4)[e]	0.41 (dd, $^{3}J_{PH^a} \approx {}^{2}J_{H^a}{}_{H^m}$ = 7.4, $C\underline{H}_2$); 1.05 (d, $^{3}J_{PH}$ = 12.0, major), 1.13 (d, $^{3}J_{PH}$ = 11.6, minor) ($C\underline{Me}_3$); 1.15 (d, $^{3}J_{PH}$ = 12.5), 1.58 (d, $^{3}J_{PH}$ = 12.6) ($C\underline{Me}_2$)
	42.9	2.06	-10.09(45.2)[g]	
[46] $\overline{RuH(CH_2CH_2CH_2}PBu^t_2)(\eta^6\text{-}C_6Me_6)$[n]	114.5	1.97	-12.35(45.2)	1.08 (d, $^{3}J_{PH}$ = 11.3), 1.16 (d, $^{3}J_{PH}$ = 11.8) ($C\underline{Me}_3$)

Table 3-1 : ^{1}H and ^{31}P NMR Data for Cyclometallated and Hydridophenyl Complexes (Cont'd)

Compound	δ(P)	δ($C_6\underline{Me}_6$)	δ(Ru$\underline{H}$) ($^{2}J_{PH}$)	Other
[47] $\overline{RuH(CH_2CHMePPr^i_2)}(\eta^6\text{-}C_6Me_6)$[f]	33.4	2.10	-9.91(46.1)[e]	0.15-0.3, 0.8-2.0 (m, CH$\underline{Me}$ and C$\underline{H}_2$), 2.6-
	21.0		-9.47(46.9)[g]	2.9, 3.2-3.4 (m, C$\underline{H}$)
[48] $\overline{RuH(CH_2CMe_2PMe_2)}(\eta^6\text{-}C_6Me_6)$[o]	-17.1	2.06	-8.07(47.9)[e]	0.45 (br dd, $^{2}J_{H_aH_m} \approx {}^{3}J_{PH_a} \approx 6$, C$\underline{H}_a\underline{H}_m$); 1.01 (d, $^{2}J_{PH}$ = 9.2, P$\underline{Me}$); 1.00 (d, $^{3}J_{PH}$ = 13.2), 1.32 (d, $^{3}J_{PH}$ = 14.7) (C$\underline{Me}_2$).
		2.11[p]	-9.17(48.4)[p,e]	0.12 (dd, $^{3}J_{PH_a}$ = 5.5, $^{2}J_{H_aH_m}$ = 7.5)[p]; 0.75 (ddd, $^{3}J_{PH_m}$ = 24.4, $^{3}J_{H_mH}Ru$ = 3.5)[p] (C$\underline{H}_2$); 0.84 (d, $^{3}J_{PH}$ = 14.3)[p], 1.01 (d, $^{3}J_{PH}$ = 14.1)[p] (C$\underline{Me}_2$); 1.02 (d, $^{2}J_{PH}$ = 10.6)[p], 1.17 (d, $^{2}J_{PH}$ = 8.7)[p] (P$\underline{Me}_2$)
[49] $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$[q]	36.1	1.88	-11.02(53.7)	0.77 (d, $^{2}J_{PH}$ = 7.9), 1.01 (d, $^{2}J_{PH}$ = 7.3) (P$\underline{Me}$); 0.87 (d, $^{3}J_{PH}$ = 13.4, C$\underline{Me}_3$); 6.9-7.8 (m, $C_6\underline{H}_5$)
[50] $\overline{RuH(\underline{o}\text{-}C_6H_4PMePh)}(\eta^6\text{-}C_6Me_6)$[f]*	-29.7	2.07	-7.87(44.6)	Predominantly $RuH_2(\eta^6\text{-}C_6Me_6)(PMePh_2)$
	-32.2	1.93	-7.70(41.5)	

Table 3-1 : ^1H and ^{31}P NMR Data for Cyclometallated and Hydridophenyl Complexes (Cont'd)

Compound	δ(P)	δ($C_6\underline{Me}_6$)	δ(Ru$\underline{H}$) ($^2J_{PH}$)	Other
[51] $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$*	24.2	1.74	-10.49(53.7)	1.03 (d, $^2J_{PH}$ = 9.2), 1.36 (d, $^2J_{PH}$ = 8.5) (P$\underline{Me}$); 7 to 8 (m, $C_6\underline{H}_5$)
[53] $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PMe_3)^r$	6.5	1.90	-10.77(56.8)	0.95 (d, $^2J_{PH}$ = 9.2, P$\underline{Me}$); 7.0 to 7.9 (m, $C_6\underline{H}_5$)

a: In C_6D_6, δ in ppm, J in Hz.

b: δ(F) = -108.8, -109.2, -110.6

c: Small coupling to F.

d: In toluene-d_8 at -10°.

e: Additional coupling of ca. 3Hz to one methylene proton.

f: Two diastereoisomers present.

g: Further couplings not resolved.

h: 1:1:1 triplet, $^2J_{PD}$ = 7Hz.

i: Also contained some $\overline{RuH(CH_2CH_2CH_2PPh_2)}(\eta^6\text{-}C_6Me_6)$ [40].

j: Contains ca. 10% $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$.

k: In toluene-d_8 at -30°.

l: In toluene-d_8.

m: Additional coupling of ca. 4Hz to two methylene protons.

n: A mixture of [45] and [46].

o: Contains ca. 30% $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$.

p: In THF-d_8.

q: Contains ca. 10% $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$.

r: Contains ca. 25% free C_6Me_6 (by ^1H NMR spectroscopy).

Table 3-2 : ^{13}C NMR Data For Cyclometallated and Hydridophenyl Complexes[a]

Compound	$\delta(\underline{C}_6Me_6)$	$\delta(C_6\underline{Me}_6)$	Other
[27] $Ru\overline{H(\underline{o}\text{-}C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$	96.8(3)	17.0	
[29] $Ru\overline{H([\underline{o}\text{-}C_6H_3\text{-}\underline{p}\text{-}F]P[\underline{p}\text{-}C_6H_4F]_2)}(\eta^6\text{-}C_6Me_6)$	97.4(0)	16.9	
[30] $Ru\overline{H([\underline{o}\text{-}C_6H_3\text{-}\underline{p}\text{-}CH_3]P[\underline{p}\text{-}C_6H_4CH_3]_2)}(\eta^6\text{-}C_6Me_6)$	96.5(3)	17.1	22.7 (0, $C_6H_3\underline{C}H_3$); 21.2 (0,$C_6H_4\underline{C}H_3$)
[31] $Ru\overline{H(CH_2CMe_2PPh_2)}(\eta^6\text{-}C_6Me_6)$	94.8(0)	17.0	11.4 (43, $\underline{C}H_2$); 30.7 (0), 30.9 (3) ($C\underline{Me}_2$); 54.6 (35, $\underline{C}Me_2$)
[32] $Ru\overline{H(\underline{o}\text{-}C_6H_4PBu^tPh)}(\eta^6\text{-}C_6Me_6)$	96.3(3)	17.0	28.0 (6, $C\underline{Me}_3$)
[33] $Ru\overline{H(CH_2CHMePPh_2)}(\eta^6\text{-}C_6Me_6)$[b]	94.6(0) 94.4(0)	16.8 17.1	-1.1 (45, major), 2.4 (42, minor) ($\underline{C}H_2$); 19.3 (0, minor), 30.2 (0, major) (PCH$\underline{Me}$); 49.1 (37,major), 52.7 (38, minor) ($\underline{C}H$)
[34] $Ru\overline{H(\underline{o}\text{-}C_6H_4PPhPr^i)}(\eta^6\text{-}C_6Me_6)$	96.3(0)	17.0	18.9 (0), 20.8 (4) ($CH\underline{Me}_2$); 28.9 (22, $\underline{C}HMe_2$)
[36] $Ru\overline{H(\underline{o}\text{-}C_6H_4PEtPh)}(\eta^6\text{-}C_6Me_6)$[b]	96.2(3) 17.6	17.0	10.3 (0, $CH_2\underline{C}H_3$); 22.3 (18, minor), 24.8 (21, major) ($\underline{C}H_2CH_3$)

Table 3-2 : ^{13}C NMR Data For Cyclometallated and Hydridophenyl Complexes (Cont'd)

Compound	$\delta(\underline{C}_6Me_6)$	$\delta(C_6\underline{Me}_6)$	Other
[38] $\overline{RuH(\underline{o}\text{-}CH_2C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$	96.3(3)	16.3	22.6 (8, $\underline{C}H_2$)
[39] $\overline{RuH(\underline{o}\text{-}C_6H_4PPhPr^n)}(\eta^6\text{-}C_6Me_6)$[b,c]	96.3(3)	17.0 (17.6)	15.8 (13, $CH_2CH_2\underline{C}H_3$); 19.9 (0,major), 30.2 (0, minor ?) ($CH_2\underline{C}H_2CH_3$); 31.8 (16, minor), 34.0 (21, major) ($\underline{C}H_2CH_2CH_3$)
[40] $\overline{RuH(CH_2CH_2CH_2PPh_2)}(\eta^6\text{-}C_6Me_6)$	95.9(3)	16.3	21.9 (7, $\overline{Ru\underline{C}H_2CH_2CH_2P}$); 33.1 (12, $\overline{Ru\underline{C}H_2CH_2CH_2P}$); 39.5 (34, $\overline{RuCH_2CH_2\underline{C}H_2P}$)
[42] $\overline{RuH(CH_2CMe_2PBu^tMe)}(\eta^6\text{-}C_6Me_6)$	93.3(0)	17.5	8.0 (6, P$\underline{Me}$); 11.9 (44, $\underline{C}H_2$); 27.8 (4, C$\underline{Me}_3$); 28.8 (0), 30.7 (4) (C$\underline{Me}_2$); 32.7 (6, $\underline{C}Me_3$); 51.8 (34, $\underline{C}Me_2$)
[43] $\overline{RuH(CH_2CMe_2PBu^tEt)}(\eta^6\text{-}C_6Me_6)$[d]	93.2(0)	17.6 17.4	11.7 (0, $CH_2\underline{C}H_3$); 12.4 (43, Ru$\underline{C}H_2$); 16.4 (4, $\underline{C}H_2CH_3$); 28.9 (4, C$\underline{Me}_3$); 30.4 (4), 30.7 (0) (C$\underline{Me}_2$); 33.6 (6, $\underline{C}Me_3$); 53.3 (32, $\underline{C}Me_2$)
[44] $\overline{RuH(CH_2CH_2PBu^t_2)}(\eta^6\text{-}C_6Me_6)$[e]	92.5(0)		34.3 (34, $\overline{RuCH_2\underline{C}H_2P}$); {-9.2 (41, $\overline{Ru\underline{C}H_2CH_2P}$) ?}

Table 3-2 : ^{13}C NMR Data For Cyclometallated and Hydridophenyl Complexes (Cont'd)

Compound	$\delta(\underline{C}_6Me_6)$	$\delta(C_6\underline{Me}_6)$	Other
[45] $Ru\overline{H(CH_2CMe_2}\overline{PBu^tPr^n)}(\eta^6\text{-}C_6Me_6)$[f]	93.3(3)	17.7	12.4 (43, $\underline{C}H_2CMe_2$); 53.3 (32, $\underline{C}Me_2$)
[46] $Ru\overline{H(CH_2CH_2CH_2}\overline{PBu^t_2)}(\eta^6\text{-}C_6Me_6)$[f]	94.6(3)	17.0	22.0 (7, $Ru\overline{CH_2\underline{C}H_2CH_2P}$); 34.7 (9, $Ru\overline{\underline{C}H_2CH_2CH_2P}$)
[47] $Ru\overline{H(CH_2CHMeP}\overline{Pr^i_2)}(\eta^6\text{-}C_6Me_6)$[b]	93.0(0) 93.3(0)	17.8 17.7	17-46 ($\underline{C}H\underline{Me}_2$, $\underline{C}H_2$)
[48] $Ru\overline{H(CH_2CMe_2}\overline{PMe_2)}(\eta^6\text{-}C_6Me_6)$[g]	94.0(3)		27.0 (0), 28.6 (4) ($C\underline{Me}_2$)
[49] $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$	97.9(0)	17.1	14.5 (18), 15.3 (29) ($P\underline{Me}$); 26.7 (6, $C\underline{Me}_3$)
[53] $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PMe_3)$[h]	97.3(3)	17.0	20.9 (31, $P\underline{Me}$)

a: In C_6D_6, δ in ppm, J_{PC} (in parentheses) in Hz. Aromatic carbons appear in the region 120-140 ppm.

b: Two diastereoisomers present.

c: Also contains $Ru\overline{H(CH_2CH_2CH_2}\overline{PPh_2)}(\eta^6\text{-}C_6Me_6)$ [40].

d: Contains ca. 10% $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$.

e: Compound not isolated; only spectroscopically characterized in toluene-d_8 at -35°. Sample predominantly [43].

f: A mixture of [45] and [46].

g: Contains 30% $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$.

h: Contains ca. 25% free C_6Me_6 (by ^1H NMR spectroscopy).

Table 3-3 : Infrared Data for Cyclometallated and Hydridophenyl Complexes[a]

Compound	ν(RuH) (cm^{-1})	Bands due to o-aryl metallation (cm^{-1})
[27] $RuH(o\text{-}C_6H_4PPh_2)(\eta^6\text{-}C_6Me_6)$	1940	1555,1413,720
[29] $RuH([o\text{-}C_6H_3\text{-}p\text{-}F]P[p\text{-}C_6H_4F]_2)(\eta^6\text{-}C_6Me_6)$	1903	
[30] $RuH([o\text{-}C_6H_3\text{-}p\text{-}CH_3]P[p\text{-}C_6H_4CH_3]_2)(\eta^6\text{-}C_6Me_6)$	1905	1555, 1410, 730
[31] $RuH(CH_2CMe_2PPh_2)(\eta^6\text{-}C_6Me_6)$	1960	
[32] $RuH(o\text{-}C_6H_4PBu^tPh)(\eta^6\text{-}C_6Me_6)$	1955	1555, 1413, 728
[33] $RuH(CH_2CHMePPh_2)(\eta^6\text{-}C_6Me_6)$	1910	
[34] $RuH(o\text{-}C_6H_4PPhPr^i)(\eta^6\text{-}C_6Me_6)$	1973	1557, 1413, 728
[36] $RuH(o\text{-}C_6H_4PEtPh)(\eta^6\text{-}C_6Me_6)$	1900(br), 1930(sh)	1555, 1410, 725
[38] $RuH(o\text{-}CH_2C_6H_4PPh_2)(\eta^6\text{-}C_6Me_6)$	1880	
[39] $RuH(o\text{-}C_6H_4PPhPr^n)(\eta^6\text{-}C_6Me_6)$	1925(br sh), 1960(br)	1555, 1412, 725
[40] $RuH(CH_2CH_2CH_2PPh_2)(\eta^6\text{-}C_6Me_6)$	1950(v br)	
[42] $RuH(CH_2CMe_2PBu^tMe)(\eta^6\text{-}C_6Me_6)$	1937	

Table 3-3 : Infrared Data for Cyclometallated and Hydridophenyl Complexes (Cont'd)

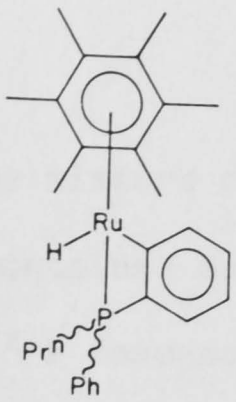
Compound	ν(RuH) (cm^{-1})	Bands due to o-aryl metallation (cm^{-1})
[43] $\overline{RuH(CH_2CMe_2PBu^tEt)}(\eta^6\text{-}C_6Me_6)$	1957	
[45] $\overline{RuH(CH_2CMe_2PBu^tPr^n)}(\eta^6\text{-}C_6Me_6)$ [b]	1965, 2000(br)	
[46] $\overline{RuH(CH_2CH_2CH_2PBu^t_2)}(\eta^6\text{-}C_6Me_6)$ [b]		
[47] $\overline{RuH(CH_2CHMePPr^i_2)}(\eta^6\text{-}C_6Me_6)$	1900, 1950(sh)	
[48] $\overline{RuH(CH_2CMe_2PMe_2)}(\eta^6\text{-}C_6Me_6)$	1895(br), 1930(br sh) 1910(br), 1945(sh) [c]	
[49] $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$	1930	
[50] $\overline{RuH(o\text{-}C_6H_4PMePh)}(\eta^6\text{-}C_6Me_6)$ [d]		1555, 1410, 730
[53] $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PMe_3)$	1940	

a: KBr disc; sh = shoulder, br = broad.

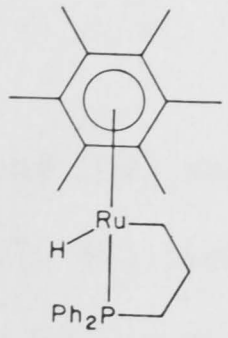
b: In n-hexane.

c: Mixture of [45] and [46].

d: Not isolated, identified by NMR and IR spectroscopy only.



[39](a,b)



[40]

7) L = PPh_2Pr^n

The reaction between $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2Pr^n)$ and methyllithium at -16° formed a mixture containing three components. The ^1H NMR spectrum of the mixture displayed hydride resonances at δ -7.90 ($^2J_{PH}$ = 43Hz), -7.94 ($^2J_{PH}$ = 43Hz) and -10.98ppm ($^2J_{PH}$ = 46Hz). The $^{31}P[^1H]$ NMR spectrum consisted of three peaks at δ -21.3, -15.8 and 79.3ppm, in the approximate ratio 1:5:2. The first two resonances were due to the two diastereoisomeric ortho-metallated complexes [39], whilst the latter were due to the five-membered ring compound [40]. When the mixture was heated in C_6D_6, the resonances due to [39] disappeared, but a new deuterium coupled resonance appeared in the $^{31}P[^1H]$ NMR spectrum at δ 52.6ppm. The coupling constant (J_{PD} = 7.3Hz) was consistent with the presence of the ruthenium deuteride species $RuD(C_6D_5)(\eta^6\text{-}C_6Me_6)(PPh_2Pr^n)$ [41-d_6], which was formed by attack on a C-D bond of C_6D_6 by the intermediate $Ru(\eta^6\text{-}C_6Me_6)(PPh_2Pr^n)$. The protio analogue $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PPh_2Pr^n)$ [41] was present in the reaction mixture formed by treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2Pr^n)$ with phenyllithium in benzene, but was not isolated. At room temperature, this reaction gave [39], [40] and [41] in a ratio of approximately 3:3:2, as estimated by ^1H NMR spectroscopy. The hydride proton of [41] resonated at δ -10.48ppm, with a coupling to phosphorus of 51.9Hz, and the hexamethylbenzene protons probably gave rise to the peak at δ

1.73ppm.

When the mixture of [39] and [40] was heated in toluene, the isolated solid contained mainly [40], but there were also other products having ^{31}P resonances at δ 52.5 and 26.5ppm. Decomposition resulted on attempting the isomerization in THF at 70°. However, heating in n-hexane and subsequent recrystallization led to pure [40], which was isolated in 47% yield.

Treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2Pr^n)$ with methyllithium at -20° and careful work-up below 10° formed a mixture of [39] and [40] in about a 3:1 ratio, which was isolated in 14% yield. The ratio of diastereoisomers of [39] varied in different preparations, but was usually 2.5:1 to 3.5:1. The infrared spectrum of this mixture showed a broad peak due to ν(RuH) at 1960cm^{-1}, with a shoulder at 1925cm^{-1}, as well as bands due to ortho-metallation {Table 3-3}. The diastereoisomers of [39] displayed distinct hexamethylbenzene, terminal methyl and hydride resonances in the ^1H spectrum. These appeared at δ 1.93, 0.81 and -7.40ppm {major isomer} and at δ 2.10, 1.12 and -7.94ppm {minor isomer} for the hexamethylbenzene, terminal methyl and hydride protons, respectively. There were also two phosphorus resonances at δ -15.8 and -21.3ppm, which show the characteristic large upfield shift of approximately 70ppm from that of the starting material. The assignment of the $^{13}C[^1H]$ NMR spectrum given in Table 3-2 is tentative, and is based on a comparison with the $^{13}C[^1H]$ NMR spectra of other n-propyl phosphine complexes prepared during this work.

The infrared spectrum of the thermodynamic product [40] showed no bands due to ortho-metallation, although there was a very

broad peak due to ν(RuH) at 1950cm^{-1}. The ^{1}H NMR spectrum displayed the methylene protons as a series of broad low intensity peaks between δ 1.0 and 2.6ppm. The chemical shift of the phosphorus nucleus at δ 79.3ppm is shifted downfield from that of RuHCl(η^6-C_6Me_6)(PPh_2Pr^n) by almost 30ppm, as expected. The ^{13}C[^{1}H] NMR spectrum of [40] showed the methylene carbon resonances as a set of doublets at δ 21.9 ($^2J_{PC}$ = 7Hz, $\overline{RuCH_2\underline{C}H_2CH_2P}$), 33.1 ($^2J_{PC}$ = 12Hz, $Ru\underline{C}H_2$) and 39.5ppm ($^1J_{PC}$ = 34Hz, $P\underline{C}H_2$).

The isomerization of [39] to [40] was monitored in a 2:1 mixture of cyclohexane and cyclohexane-d_{12} at 60° by ^{31}P[^{1}H] NMR spectroscopy. The sample used for this isomerization contained impurities having resonances at δ 71.8, 53.8 ,25.5, -24.3 and -30.8ppm in the ^{31}P[^{1}H] NMR spectrum. The intensities of some of these resonances varied during the course of the experiment. Furthermore, when a sample of [39] and [40] which was free of these impurities was heated at 60° {to obtain spectra to test for NOE and T_1 effects}, the resonances at δ 71.8, 25.5 and -24.3ppm slowly formed. None of these species showed coupling to deuterium. The contaminants were clearly by-products of the isomerization reaction, and may have included four-membered ring alkyl metallated species such as $\overline{RuH(CHMeCH_2PPh_2}$)($\eta^6$-$C_6Me_6$). The presence of the impurities was ignored in the analysis of the kinetic data, as they did not behave in a readily understood or reproducible manner. In addition, there appeared to be a significant difference in NOE between the ^{31}P resonances of the major diastereoisomer [39a] and the product [40]. The raw data were multiplied by the appropriate factors to compensate for the NOE contributions. Thus the kinetic data for this isomerization were not very reliable. The isomerization of [39] to [40] was first order at 60° {Figure 3-9}, with rate constants of (2.0 ± 0.1) x 10^{-5} s^{-1} and

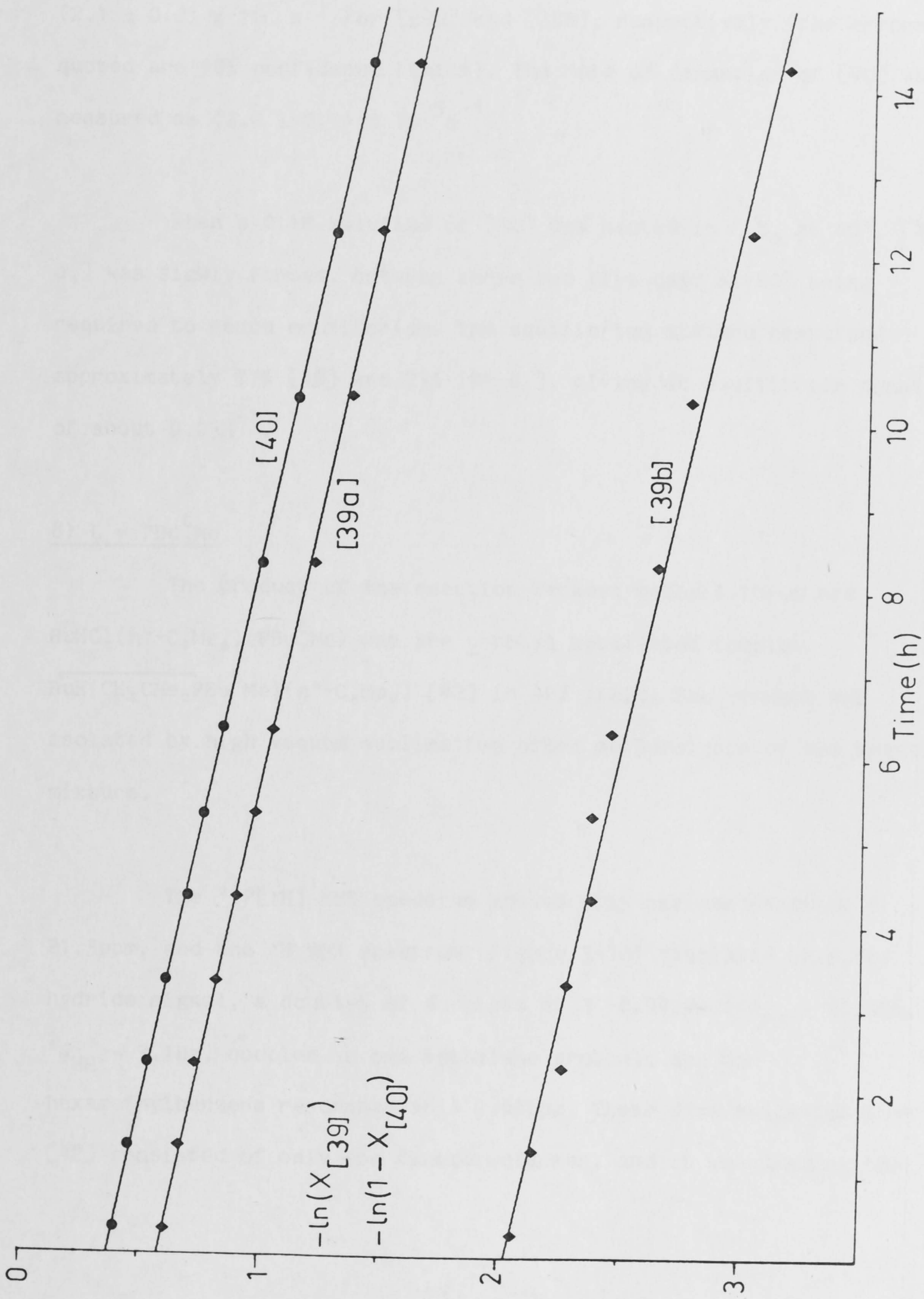


Figure 3-9: Plot of data for the isomerization of $\overline{RuH(\underline{o}\text{-}\overline{C_6H_4}PPhPr^n)}(\eta^6\text{-}C_6Me_6)$ [39] into $\overline{RuH(CH_2CH_2CH_2PPh_2)}(\eta^6\text{-}C_6Me_6)$ [40], including lines of best fit. For explanation of symbols, see appendix 2, p188.

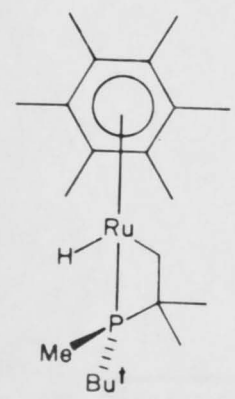
$(2.1 \pm 0.2) \times 10^{-5} s^{-1}$ for [39a] and [39b], respectively {the errors quoted are 90% confidence limits}. The rate of formation of [40] was measured as $(2.0 \pm 0.1) \times 10^{-5} s^{-1}$.

When a 0.1M solution of [40] was heated in C_6D_6 at 60°, [41-d_6] was slowly formed, between three and five days at 60° being required to reach equilibrium. The equilibrium mixture contained approximately 77% [40] and 23% [41-d_6], giving an equilibrium constant of about $0.03M^{-1}$.

8) L = PBu^t_2Me

The product of the reaction between methyllithium and $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Me)$ was the t-butyl metallated complex $\overline{RuH(CH_2CMe_2PBu^tMe)}(\eta^6\text{-}C_6Me_6)$ [42] in 42% yield. The product was isolated by high vacuum sublimation after methanolysis of the reaction mixture.

The $^{31}P[^1H]$ NMR spectrum showed only one resonance at δ 21.3ppm, and the ^1H NMR spectrum {Figure 3-10} displayed only one hydride signal, a doublet of doublets at δ -8.94ppm ($^2J_{PH}$ = 46.4Hz, $^3J_{HH}$ = 3.1Hz, coupled to one methylene proton), and one hexamethylbenzene resonance at δ 2.05ppm. These data suggested that [42] consisted of only one diastereoisomer, and it was assumed that



[42]

Figure 3-10: ^1H NMR spectrum of $\overline{RuH(CH_2CMe_2PBu^tMe)}(\eta^6\text{-}C_6Me_6)$ [42].

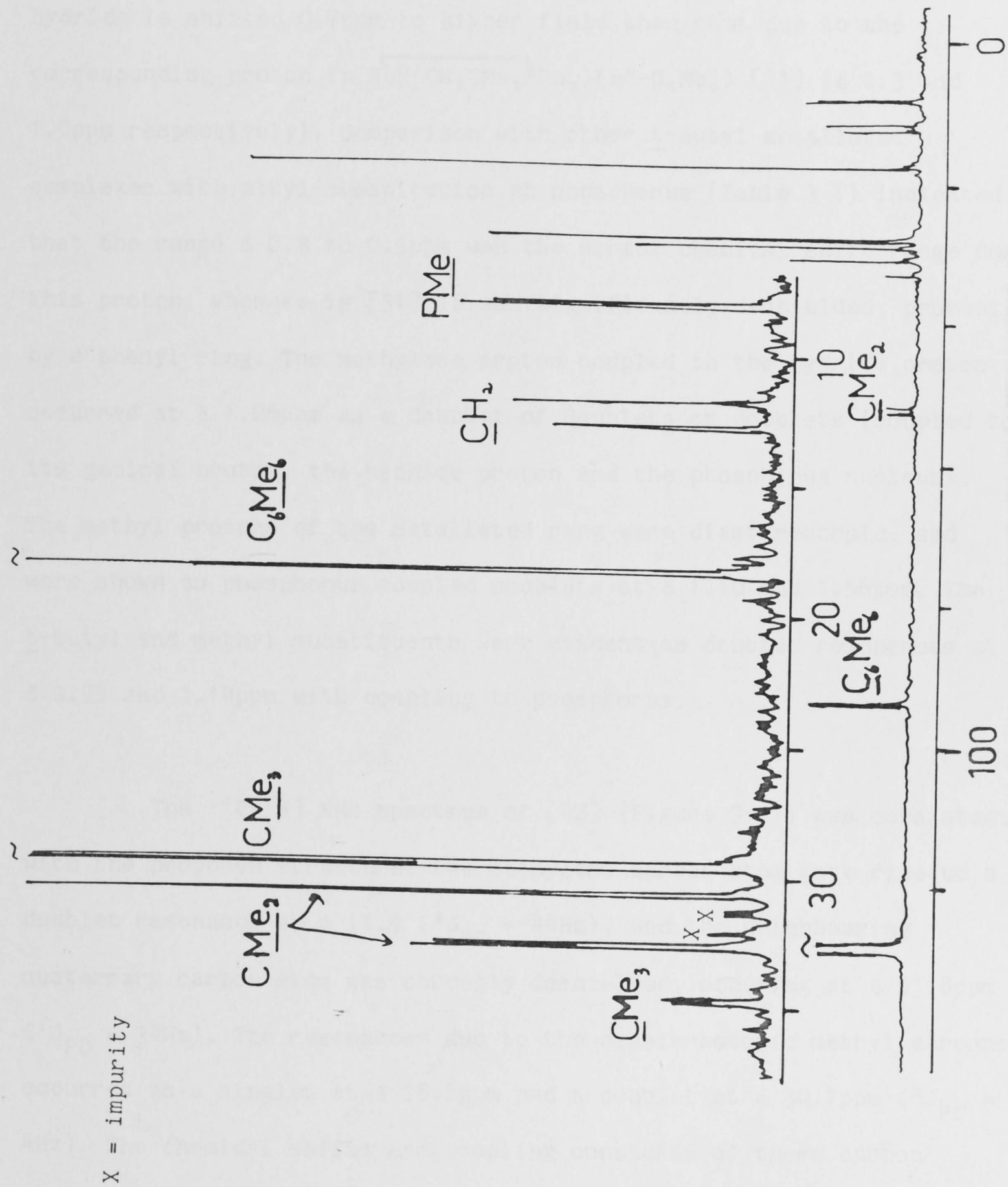


Figure 3-11: $^{13}C[^{1}H]$ NMR spectrum of $\overline{RuH(CH_2CMe_2PBu^tMe)}(\eta^6\text{-}C_6Me_6)$ [42].

the isomer formed had the less bulky methyl group pointing towards the arene ring. The peak due to the methylene proton not coupled to hydride is shifted 0.7ppm to higher field than that due to the corresponding proton in $\overline{RuH(CH_2CMe_2PPh_2)}(\eta^6\text{-}C_6Me_6)$ [31] {δ 0.3 and 1.0ppm respectively}. Comparison with other t-butyl metallated complexes with alkyl substitution at phosphorus {Table 3-1} indicated that the range δ 0.3 to 0.5ppm was the normal chemical shift range for this proton, whereas in [31] it was significantly deshielded, probably by a phenyl ring. The methylene proton coupled to the hydride proton occurred at δ 1.26ppm as a doublet of doublets of doublets {coupled to its geminal proton, the hydride proton and the phosphorus nucleus}. The methyl protons of the metallated ring were diastereotopic, and were shown as phosphorus coupled doublets at δ 1.10 and 1.56ppm. The t-butyl and methyl substituents were evident as doublet resonances at δ 0.99 and 1.14ppm with coupling to phosphorus.

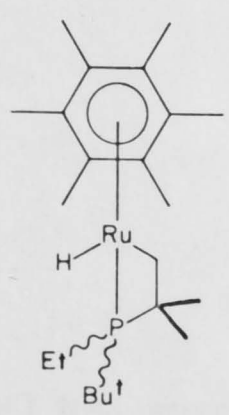
The $^1H[^{13}C]$ NMR spectrum of [42] {Figure 3-11} was consistent with the proposed structure: the methylene carbon atom gave rise to a doublet resonance at δ 11.9 ($^2J_{PC}$ = 44Hz), and the neighbouring quaternary carbon atom was strongly deshielded, occuring at δ 51.8ppm ($^1J_{PC}$ = 34Hz). The resonances due to the diastereotopic methyl carbons occurred as a singlet at δ 28.8ppm and a doublet at δ 30.7ppm ($^2J_{PC}$ = 4Hz). The chemical shifts and coupling constants of these carbon nuclei were very close to the analogous carbons in $\overline{RuH(CH_2CMe_2PPh_2)}(\eta^6\text{-}C_6Me_6)$ [31]. The resonances at δ 8.0 ($^1J_{PC}$ = 6Hz), 27.8 ($^2J_{PC}$ = 4Hz) and 32.7ppm ($^1J_{PC}$ = 6Hz) were assigned to the phosphine methyl, t-butyl methyl and quaternary carbon nuclei, respectively.

The peaks marked in the ^1H and $^1H[^{13}C]$ NMR spectra of [42]

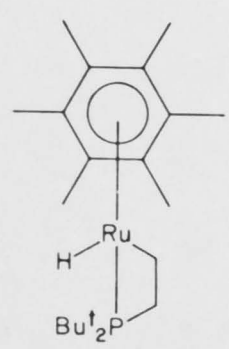
{Figures 3-10 and 3-11} were probably due to an impurity which also gave rise to a barely detectable hydride resonance in the ^{1}H NMR spectrum at δ -11.80 (d, $^2J_{PH}$ = 41.5Hz). The impurity was probably the dihydride $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^t_2Me)$. There was no indication of the formation of a methyl metallated complex in the synthesis of [42].

9) L = PBu^t_2Et

The reaction between $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$ and methyllithium below -10° for two and a half hours was incomplete. The main component of the mixture was the starting material. However, two new hydride resonances appeared in the ^{1}H NMR spectrum at δ -9.42 (a doublet of doublets) and -9.52ppm (a doublet of triplets) in the approximate ratio 1.4:1. There was also a barely detectable doublet hydride resonance at δ -10.17ppm ($^2J_{PH}$ = 45.2Hz). Heating of the mixture overnight caused the hydride resonance at δ -9.52ppm to disappear. When the reaction was performed at room temperature, it proceeded to completion, and only a very small quantity of the hydride resonating at δ -10.17ppm and the dihydride (δ -12.52ppm) were formed. None of the compound giving rise to the hydride resonance at δ -9.52ppm was detected. The product isolated after purification by subliming twice under high vacuum at 110° was the t-butyl metallated complex $\overline{RuH(CH_2CMe_2PBu^t}Et)(\eta^6\text{-}C_6Me_6)$ [43]. Two diastereoisomers in the ratio 11:1 were observed for [43], in which the ruthenium and



[43](a,b)



[44]

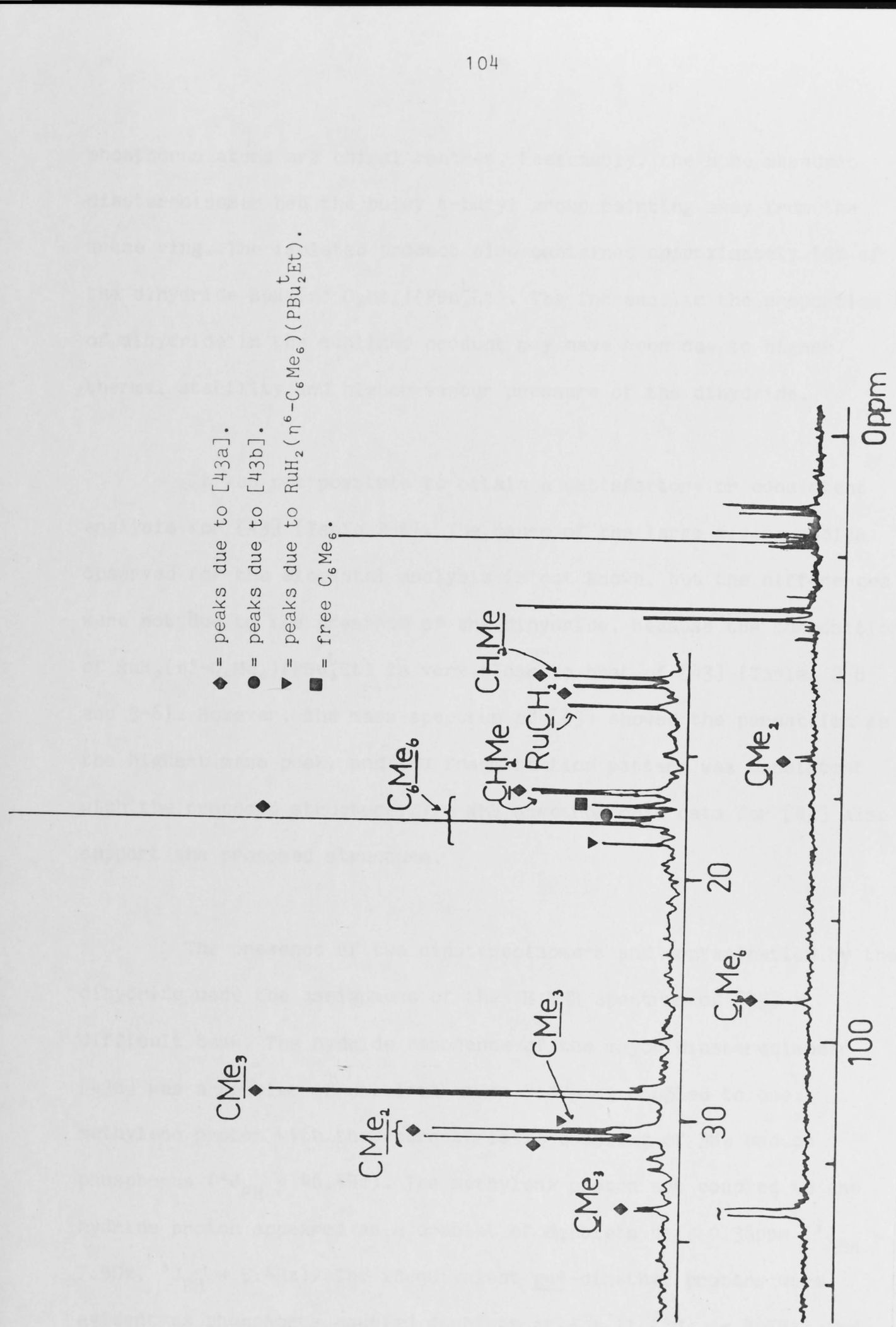


Figure 3-12: $^{1}{}^{3}C[^{1}H]$ NMR spectrum of $\overline{RuH(CH_2CMe_2PBu^tEt)}(\eta^6-C_6Me_6)$ [43].

phosphorus atoms are chiral centres. Presumably, the more abundant diastereoisomer had the bulky t-butyl group pointing away from the arene ring. The isolated product also contained approximately 10% of the dihydride $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$. The increase in the proportion of dihydride in the sublimed product may have been due to higher thermal stability and higher vapour pressure of the dihydride.

It was not possible to obtain a satisfactory or consistent analysis for [43] {Table 3-6}. The cause of the large discrepancies observed for the elemental analysis is not known, but the differences were not due to the presence of the dihydride, because the composition of $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$ is very close to that of [43] {Tables 2-8 and 3-6}. However, the mass spectrum of [43] showed the parent ion as the highest mass peak, and the fragmentation pattern was consistent with the proposed structure. The NMR spectroscopic data for [43] also support the proposed structure.

The presence of two diastereoisomers and contamination by the dihydride made the assignment of the ^1H NMR spectrum of [43] a difficult task. The hydride resonance of the major diastereoisomer [43a] was a doublet of doublets at δ -9.42ppm, coupled to one methylene proton with the characteristic coupling of 3Hz and to phosphorus ($^2J_{PH}$ = 46.4Hz). The methylene proton not coupled to the hydride proton appeared as a doublet of doublets at δ 0.38ppm ($^2J_{HH}$ = 7.5Hz, $^3J_{PH}$ = 5.4Hz). The inequivalent gem-dimethyl protons were evident as phosphorus coupled doublets at δ 1.11 ($^3J_{PH}$ = 4.7Hz) and 1.58ppm ($^3J_{PH}$ = 12.7Hz). The coupling constant of the former {4.7Hz} is uncharacteristically low. The t-butyl and terminal ethyl protons were found to be a doublet at δ 1.05ppm ($^3J_{PH}$ = 12.2Hz) and a triplet at 1.18ppm ($^3J_{HH}$ = 7.7Hz) respectively. The hexamethylbenzene protons

appeared as a singlet at δ 2.07ppm. The remaining resonances could not be unambiguously assigned. The only resonances of the minor diastereoisomer [43b] which could be assigned with any confidence were the hydride resonance at δ -10.09ppm (broadened doublet, $^{2}J_{PH}$ = 45.2Hz) and the hexamethylbenzene resonance at δ 2.06ppm.

In contrast, assignment of the $^{13}C[^{1}H]$ NMR spectrum of [43] was much more straightforward {Figure 3-12, Table 3-2}. The characteristic resonances of a metallated t-butyl group were evident {metallated methyl carbon, δ 12.4ppm ($^{2}J_{PC}$ = 43Hz); quaternary carbon, δ 53.3ppm ($^{1}J_{PC}$ = 32Hz); ring methyls, a singlet at δ 30.7ppm, a doublet at δ 30.4ppm ($^{2}J_{PC}$ = 4Hz)}. The spectrum showed the t-butyl carbon resonances at δ 28.9 ($^{2}J_{PC}$ = 4Hz) and 33.6ppm ($^{1}J_{PC}$ = 6Hz, quaternary carbon), and the ethyl carbon signals at δ 16.4 ($^{1}J_{PC}$ = 4Hz) and 11.70ppm (singlet, terminal carbon). The only resonance of [43b] which could be assigned with confidence was that due to the hexamethylbenzene methyl carbons at δ 17.4ppm. Some resonances due to the dihydride were evident {$C_6\underline{Me}_6$, $C\underline{Me}_3$ resonances at δ 18.5 and 30.3ppm (d, $^{2}J_{PC}$ = 6Hz)}. Some low intensity resonances have not been assigned. These may be due to [43b] but this could not be readily verified. The $^{31}P[^{1}H]$ NMR spectrum of the mixture showed singlet resonances at δ 36.8, 42.9 and 97.4ppm due to [43a], [43b], and the dihydride respectively.

Treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$ with methyllithium at -20° for three hours and then at -10° for three hours followed by careful work-up and attempted low temperature recrystallization from n-hexane gave a filtrate, which, on evaporating to dryness, deposited a brown powder. The brown powder was a mixture containing 15% of the product which gave rise to the doublet of triplets hydride resonance

at δ -9.52ppm, and 10% of the dihydride $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$. The remainder of the mixture was [43]. The hydride signal at δ -9.52ppm was assigned to the ethyl metallated complex $\overline{RuH(CH_2CH_2PBu^t_2)}(\eta^6\text{-}C_6Me_6)$ [44]. This was based on the observation that the hydride signal of [44] is coupled equally to two protons with a coupling constant of approximately 4Hz, as well as to phosphorus. This was more compatible with structure [44] than the alternative three-membered ring structure $\overline{RuH(CHMePBu^t_2)}(\eta^6\text{-}C_6Me_6)$. Due to the low concentration of [44] in the isolated mixture, and the complexity of the ^1H NMR spectrum, other ligand resonances of [44] could not be assigned. The $^{31}P[^1H]$ NMR spectrum of the mixture at -30° showed a singlet at δ 33.8ppm, which disappeared on allowing the sample to stand at room temperature for 40h. The chemical shift of δ 33.8ppm was 46ppm upfield from that of the starting material, consistent with the presence of a four-membered ring containing phosphorus.[67]

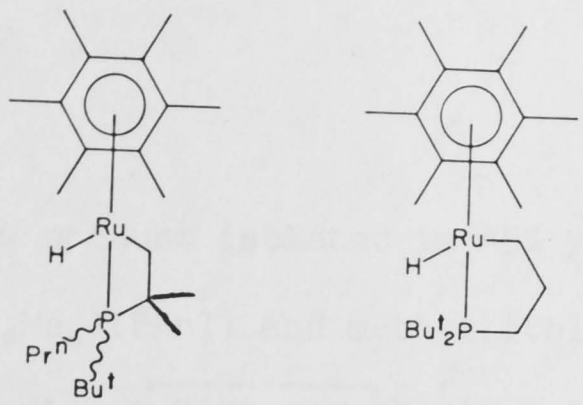
The $^{13}C[^1H]$ NMR spectrum of the mixture was very complex and very difficult to interpret. However, several resonances were present in the sample initially, but had disappeared after the sample had been allowed to stand at room temperature for 40h: a low intensity resonance at δ 92.5ppm {due to $\underline{C}_6Me_6$} and a doublet at δ 34.3ppm (J_{PC} = 34Hz) which was assigned to a CH_2 group on the basis of an INEPT spectrum at -35°. A low-intensity inverted doublet at δ -9.2ppm (J_{PC} = 41Hz) {which must be due to a CH_2 group according to the pulse sequence used} was present in the INEPT spectrum at -35°. This signal was not observed in the standard $^{13}C[^1H]$ NMR spectrum, because its chemical shift was just outside the spectral range used to obtain the standard $^{13}C[^1H]$ NMR spectrum. It was also absent in NMR spectra obtained after isomerization was complete. The chemical shift changes for these two peaks {approximately 15ppm downfield from similar CH_2

carbons for the signal at δ 34.3ppm, about 20ppm upfield from $PCH_2\underline{C}H_3$ carbons for the resonance at δ -9.2ppm} and the large phosphorus-carbon couplings {34 and 41Hz respectively} are reminiscent of the $\overline{RuCH_2CMe_2P}$ rings already encountered, and suggested that [44] contains a $\overline{RuCH_2CH_2P}$ ring. While the $^{13}C[^1H]$ NMR spectroscopic evidence was not conclusive, the proposed structure was clearly favoured by the ^1H $^{31}P[^1H]$ NMR spectroscopic evidence and the ready isomerization of [44] to [43].

10) L = $PBu^t_2Pr^n$

The reaction between $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Pr^n)$ and methyllithium at -13° for one and a half hours did not go to completion. There were three new hydride resonances at δ -10.08 (a low intensity broad doublet), -9.45 (a doublet of doublets) and -12.35ppm (a doublet), of approximately equal intensity. There were corresponding new resonances at δ 36.8, 42.9 and 114.5ppm in the $^{31}P[^1H]$ NMR spectrum. The first two signals were due to the diastereoisomers [45a] and [45b] arising from the metallation of one of the t-butyl groups. The last resonance was due to [46], derived from metallation of the terminal carbon of the propyl group. When the reaction was carried out at room temperature, a pale yellow powder was isolated by high vacuum sublimation in 57% yield. It consisted of the two diastereoisomers of [45] {both the ruthenium and phosphorus atoms are chiral centres} and [46], in the ratio 66% [45a], 8% [45b] and 26% [46]. When the mixture was heated to reflux in n-hexane for 1.5 days, an equilibrium mixture of approximately 40% [45a], 5% [45b] and 55% [46] was obtained.

The ^1H NMR spectrum of the mixture of [45] and [46] was assigned by selectively decoupling the phosphorus nuclei of [45] and



[45](a,b) [46]

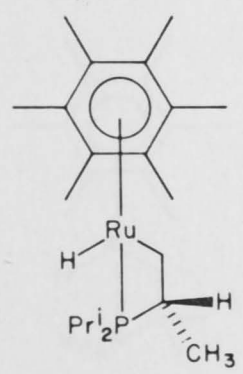
[46] in turn. The characteristic resonances for a metallated t-butyl group were observed for [45a]: one methylene proton at δ 0.41ppm as a doublet of doublets ($^3J_{PH} \approx {}^2J_{HH}$ = 7Hz) and diastereotopic ring methyl protons at δ 1.15 ($^3J_{PH}$ = 12.5Hz) and 1.58ppm ($^3J_{PH}$ = 12.6Hz). The resonances due to the remaining methylene proton and the propyl group could not be assigned. The t-butyl group of [45a] occurred as a doublet at δ 1.05ppm ($^3J_{PH}$ = 12.0Hz) and the hydride resonance was a doublet of doublets at δ -9.45ppm with a coupling to one proton of 3Hz, as well as coupling to phosphorus. The only resonances of [45b] which could be assigned were a doublet due to the non-metallated t-butyl group at δ 1.13ppm ($^3J_{PH}$ = 11.6Hz) and a broad doublet due to the hydride at δ -10.09ppm ($^2J_{PH}$ = 45.2Hz). The t-butyl groups of [46] are diastereotopic, and were evident as doublets at δ 1.08 ($^3J_{PH}$ = 11.8Hz) and δ 1.16ppm ($^3J_{PH}$ = 11.8Hz). The hydride resonance appeared as a slightly broadened doublet at δ -12.35ppm ($^2J_{PH}$ = 45.2Hz). It was not possible to assign resonances due to the metallated propyl group. The $^{13}C[^1H]$ NMR spectrum of the mixture was equally difficult to assign. The characteristic resonances for a metallated t-butyl group were present at δ 12.4 ($^2J_{PC}$ = 43Hz) and 53.3ppm ($^1J_{PC}$ = 32Hz) for the metallated and quaternary carbon nuclei of [45a] respectively. The assignments of the carbon resonances to [46] at δ 34.7 ($^2J_{PC}$ = 9Hz, Ru$\underline{C}H_2$) and 22.0ppm ($^2J_{PC}$ = 7Hz, $\overline{RuCH_2\underline{C}H_2CH_2P}$) were made by comparison

with the $^{13}C[^1H]$ NMR spectrum of $\overbrace{RuH(CH_2CH_2CH_2PPh_2)}(\eta^6\text{-}C_6Me_6)$ [40].

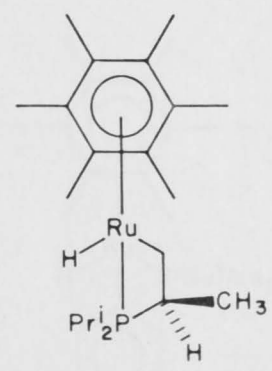
11) L = PPr^i_3

The yellow product isolated in 45% yield from the reaction between $RuHCl(\eta^6\text{-}C_6Me_6)(PPr^i_3)$ and methyllithium was the cyclometallated complex $\overbrace{RuH(CH_2CHMePPr^i_2)}(\eta^6\text{-}C_6Me_6)$ [47]. The infrared spectrum of [47] showed a broad band at 1900cm^{-1} with a shoulder at 1950cm^{-1} due to ν(RuH). There were two hydride resonances in the ^1H NMR spectrum at δ -9.91ppm (doublet of doublets, $^2J_{PH}$ = 46Hz, $^3J_{HH}$ = 2.5Hz) and -9.47 (broad doublet, $^2J_{PH}$ = 47Hz), and there were two singlets at δ 33.4 and 21.0ppm in a ratio of about 2:1 in the $^{31}P[^1H]$ NMR spectrum arising from the diastereoisomers [47a] and [47b]. The more abundant diastereoisomer presumably has the metallacyclic methyl group pointing away from the arene ligand. The ^1H and $^{13}C[^1H]$ NMR spectra of [47] were very complex in the isopropyl region because each diastereoisomer {[47a] and [47b]} has inequivalent isopropyl groups and methylene protons.

Kletzin and Werner[124] have prepared the analogous benzene complex $\overbrace{RuH(CH_2CHMePPr^i_2)}(\eta^6\text{-}C_6H_6)$ by photolysis of $RuH_2(\eta^6\text{-}C_6H_6)(PPr^i_3)$ in cyclohexane. This cyclometallated complex was reported to react with benzene to form the hydridophenyl complex $RuH(C_6H_5)(\eta^6\text{-}C_6H_6)(PPr^i_3)$, presumably by oxidative addition of



[47a]

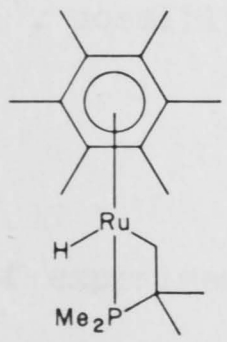


[47b]

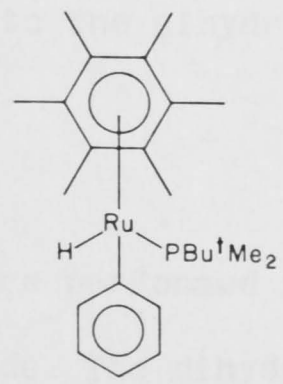
benzene to $Ru(\eta^6\text{-}C_6H_6)(PPr^i_3)$. In contrast, the hexamethylbenzene complex [47] was inert towards aromatic solvents, as shown by its synthesis in toluene solvent. Ligands such as PPr^i_3, PPh_3, CO {at 1 atm} and C_2H_4 {at 1 atm} also did not react with [47], presumably because steric strain made formation of the species $Ru(\eta^6\text{-}C_6Me_6)(PPr^i_3)L$ highly unfavourable.

12) L = PBu^tMe_2

Reaction between $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ and methyllithium in toluene gave a mixture of products. The ^1H NMR spectrum showed a series of hydride resonances assigned to the t-butyl metallated complex [48], the dihydride $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ and two aryl hydride species. When the reaction was carried out in ether, the solid isolated by vacuum sublimation contained two species, one of which was [48]. The second product apparently resulted from ether cleavage, as it was only formed when diethyl ether was used as the reaction medium. Traces of the dihydride were also present. When n-hexane was used in place of diethyl ether, the main product was [48], although significant quantities of the dihydride $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ were also formed. After purification by two high vacuum sublimations, the dihydride usually comprised 25-30% of the product. Complex [48] was a very air-sensitive solid, which had to be handled under a rigorously inert atmosphere.



[48]



[49]

The presence of the dihydride in samples of [48] hampered the complete assignment of the ^1H and $^{13}C[^1H]$ NMR spectra of [48]. In the ^1H NMR spectrum of [48] in C_6D_6, the resonances due to the phosphorus methyl protons were accidentally equivalent, appearing at δ 1.01ppm as a doublet ($^3J_{PH}$ = 9.2Hz). One of the ring methyl groups of [48] was also accidentally equivalent with the dihydride t-butyl resonance {δ 1.00ppm ($^3J_{PH}$ = 13.2Hz)}. However, the ^1H NMR spectrum of [48] in THF-d_8 showed separate resonances for each group, including those of the dihydride {Figure 3-13}. The assignment of this spectrum was made by selectively decoupling the phosphorus nuclei of [48], $RuH_2(\eta^6$-$C_6Me_6)(PBu^tMe_2)$, and the hydride nucleus of [48] {Figure 3-14}. The characteristics of t-butyl group metallation were evident in these spectra: the methylene protons appeared as a doublet of doublets at δ 0.12ppm and a doublet of doublets of doublets at δ 0.75ppm. The methyl groups of the metallated t-butyl group were diastereotopic {δ 0.84 and 1.01ppm}, as were the phosphine methyl protons {δ 1.02 and 1.17ppm}. The hydride resonance of [48] in THF-d_8 at δ -9.17ppm was shifted considerably upfield from its position in C_6D_6 {δ -8.07ppm}, and was coupled to a methylene ring proton ($^3J_{PH}$ = 3Hz) in addition to coupling to phosphorus. The $^{13}C[^1H]$ NMR spectrum was not readily assigned. The ^{31}P resonance of [48] at δ -17.1ppm was shifted 50ppm upfield from that of $RuHCl(\eta^6$-$C_6Me_6)(PBu^tMe_2)$, indicating the presence of a four-membered ring containing phosphorus. The band due to ν(RuH) in the infrared spectrum appeared at 1910cm^{-1}, and there was also a shoulder at 1945cm^{-1}, possibly due to the dihydride present in the sample.

A number of experiments were performed in an attempt to determine the origin of the dihydride. The dihydride was present when $RuHCl(\eta^6$-$C_6Me_6)(PBu^tMe_2)$ in tetramethylsilane was treated with

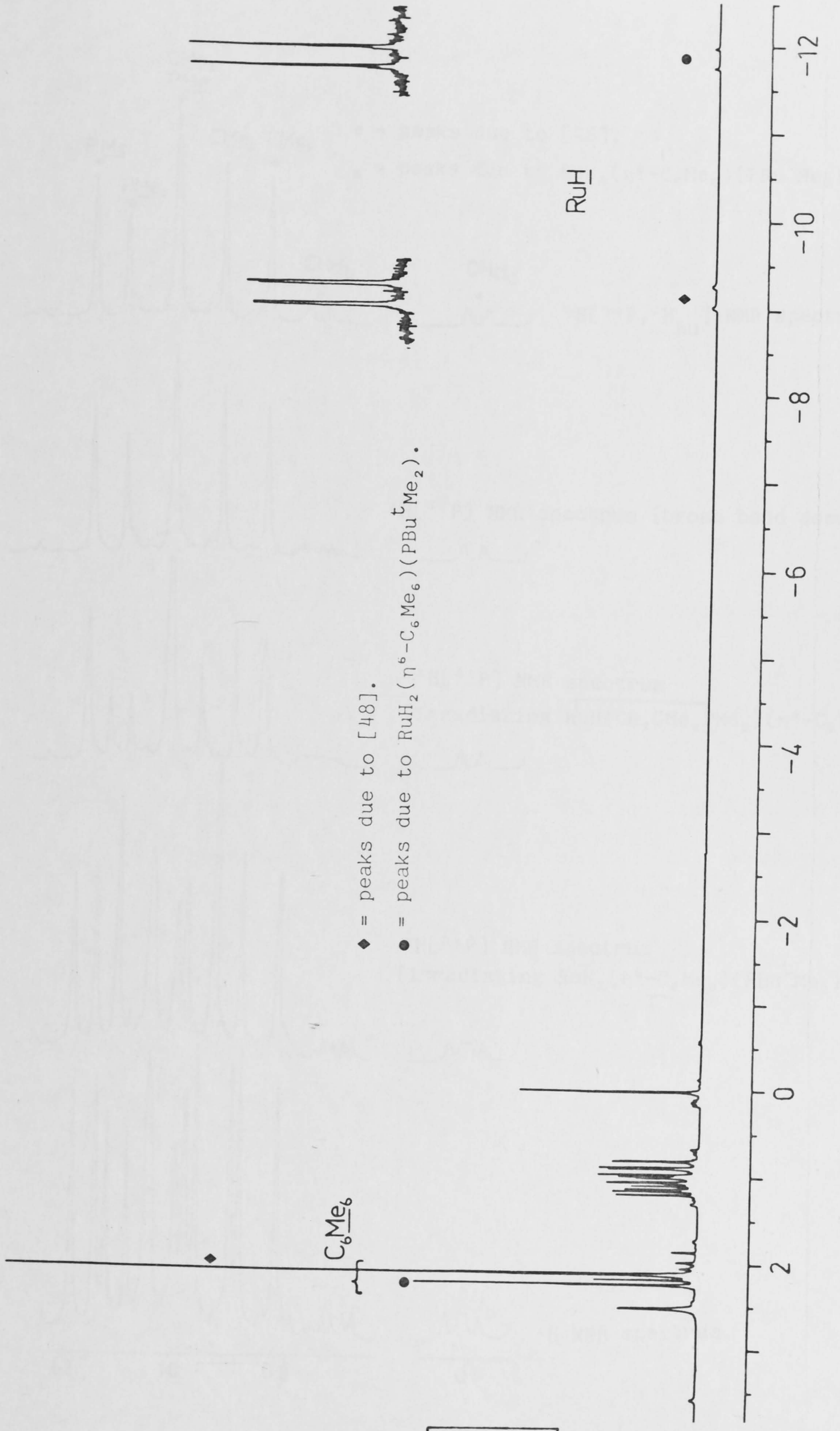
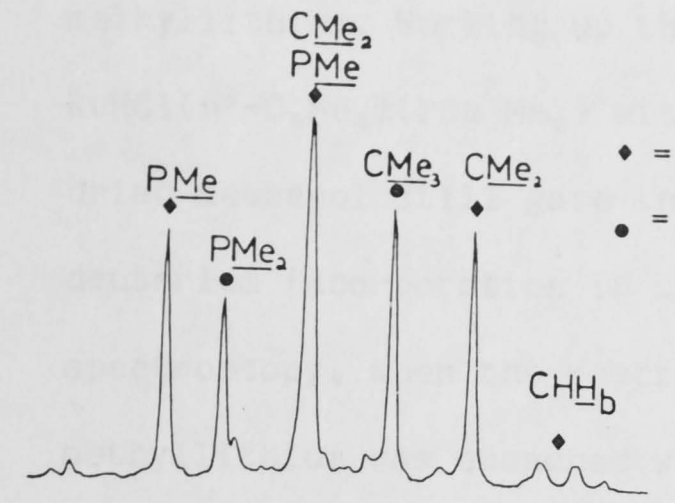


Figure 3-13: ^1H NMR spectrum of $RuH(CH_2CMe_2PMe_2)(\eta^6-C_6Me_6)$ [48] in $THF-d_8$.



◆ = peaks due to [48].

● = peaks due to $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$.

$^1H[^{31}P, ^1H_{Ru}]$ NMR spectrum.

$^1H[^{31}P]$ NMR spectrum {broad band decoupled}.

$^1H[^{31}P]$ NMR spectrum
{irradiating $\overline{RuH(CH_2CMe_2PMe_2)}(\eta^6\text{-}C_6Me_6)$}.

$^1H[^{31}P]$ NMR spectrum
{irradiating $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$}.

^1H NMR spectrum.

1·2 1·0 0·8 0·1

Figure 3-14: Selectively decoupled ^1H NMR spectra of $\overline{RuH(CH_2CMe_2PMe_2)}(\eta^6\text{-}C_6Me_6)$ [48] in THF-d_8.

methyllithium. Working up the reaction mixture formed by treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ with methyllithium in n-hexane with carefully dried methanol still gave the dihydride. There was no detectable deuterium incorporation in the dihydride, as shown by $^{31}P[^1H]$ NMR spectroscopy, when the reaction of $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ with methyllithium was quenched with CD_3OD. If $RuHD(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ had been formed, a 1:1:1 triplet at δ 42.5ppm ($^2J_{PD} \approx 7Hz$) would have been expected for this species in the $^{31}P[^1H]$ NMR spectrum. Lithium methoxide and lithium ethoxide did not react with $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ in n-hexane/diethyl ether.

Attempts to find alternative methylating agents in place of methyllithium were as unsuccessful for $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ as they had been in the case of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$. Trimethylaluminium apparently reacted with $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$: the solution effervesced, became turbid and changed colour from orange to pale yellow. However, after work-up, the crude reaction mixture contained mainly the starting material. There was a small doublet resonance at δ -0.05ppm (J_{PH} = 6.1Hz) in the ^1H NMR spectrum of the mixture, which may have been due to the methyl ligand of the species $RuMe_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$. Treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ with lithium dimethylcuprate led to extensive decomposition, and the main organometallic product appeared to be the dimethyl species $RuMe_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ {^1H NMR: δ 1.73ppm ($C_6\underline{Me}_6$); δ -0.05ppm (d, $^3J_{PH}$ = 6.1Hz, Ru$\underline{Me}$)}. The reaction of $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ with dimethylzinc was incomplete and a mixture of unidentified products was formed.

The aryl hydride species detected when $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ was treated with methyllithium in toluene were

probably tolyl hydrides arising from cleavage of the meta and para C-H bonds of toluene by the presumed intermediate $Ru(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$. Analogously, irradiation of $RhH_2(\eta^5\text{-}C_5Me_5)(PMe_3)$ in toluene at 25° produced only the meta and para isomers of the compound $RhH(C_6H_4CH_3)(\eta^5\text{-}C_5Me_5)(PMe_3)$.[111] The chemical shifts and coupling constants of the two ruthenium hydridotolyl complexes, at δ -10.88 ($^2J_{PH}$ = 53.1Hz) and -11.02ppm ($^2J_{PH}$ = 55.5Hz), were similar to the corresponding values for $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ [49] {δ -11.02ppm ($^2J_{PH}$ = 53.7Hz)}.

The ^{1}H NMR resonances which were due to the second product formed by the action of methyllithium on $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ in diethyl ether occurred at δ 1.93 ($C_6\underline{Me}_6$), 0.93 (d, $^3J_{PH}$ = 12.2Hz, $C\underline{Me}_3$), 0.81 (d, $^2J_{PH}$ = 6.7Hz, $P\underline{Me}_2$), 1.46 (broadened triplet, J = 8.2Hz) and 0.29ppm (singlet) {The last peak may be due to slight contamination by silicone grease}. The phosphorus resonance occurred at δ 22.5ppm, and the $^{13}C[^1H]$ NMR spectrum had resonances at δ 92.3 (d, $^2J_{PC}$ = 3Hz, $\underline{C}_6Me_6$), 25.5 (d, $J_{PC} \approx$ 4Hz), 16.5 (s, $C_6\underline{Me}_6$), 11.2ppm (d, J_{PC} = 19Hz), which were probably due to this species. This product may have been the ethylene complex $Ru(\eta^6\text{-}C_6Me_6)(\eta^2\text{-}C_2H_4)(PBu^tMe_2)$, in which the ethylene ligand was derived from ether cleavage. The NMR data support this proposal: the ethylene complexes $Ru(\eta^6\text{-}C_6Me_6)(\eta^2\text{-}C_2H_4)L$ were reported to have $\delta(^{31}\underline{P})$ 30.6ppm and $\delta(C_2\underline{H}_4)$ 1.70-1.78ppm (multiplet) for L = PPh_2Me, and $\delta(^{31}\underline{P})$ 21.2ppm and $\delta(C_2\underline{H}_4)$ 1.74ppm (multiplet) for L = PBu^n_3.[97]

When a solution of [48] in C_6D_6 was allowed to stand for one day, the resonances assigned to [48] disappeared, and a new 1:1:1 triplet appeared in the $^{31}P[^1H]$ NMR spectrum at δ 36.6ppm ($^2J_{PD}$ ca. 8Hz). This was assigned to $RuD(C_6D_5)(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ [49-d_6], which

was formed by attack of [48] on solvent C-D bonds. The protio analogue, $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ [49] was prepared by two independent routes: the reaction of [48] with C_6H_6, and by treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ with phenyllithium.

When $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ in diethyl ether was treated with phenyllithium, three products were observed by ^1H NMR spectroscopy: the t-butyl metallated complex [48], the hydridophenyl complex [49] and the compound presumably formed by ether cleavage. The last of these was identical with that obtained in the reaction of $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ with methyllithium in ether {see above}. Treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ in benzene with commercial phenyllithium formed [49] with a small quantity of the dihydride $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$. The aromatic region of the ^1H NMR spectrum integrated for approximately 2.5 phenyl groups per ruthenium. A white powder, probably biphenyl, sublimed with the yellow product. Commercial phenyllithium {supplier: EGA-Chemie} was found to contain significant quantities of biphenyl, terphenyl and tetraphenyl.

The reaction of $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ in benzene with phenyllithium prepared by literature methods[74] gave [49] contaminated with some $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ and $RuHBr(\eta^6\text{-}C_6Me_6)(Bu^tMe_2)$ {δ(RuH) -10.00ppm ($^2J_{PH}$ = 57.4); δ(P) 30.1ppm}. The hydridobromide was probably formed by halide metathesis of the starting material with lithium bromide present in the phenyllithium solution. The sample of [49] which was prepared by treating [48] with benzene was contaminated with approximately 7% of $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$. In both cases, [49] was isolated by two sublimations of the crude product. Despite the impurities, satisfactory analyses were obtained for samples prepared by both routes. Like [48], [49] was a very air-sensitive solid which

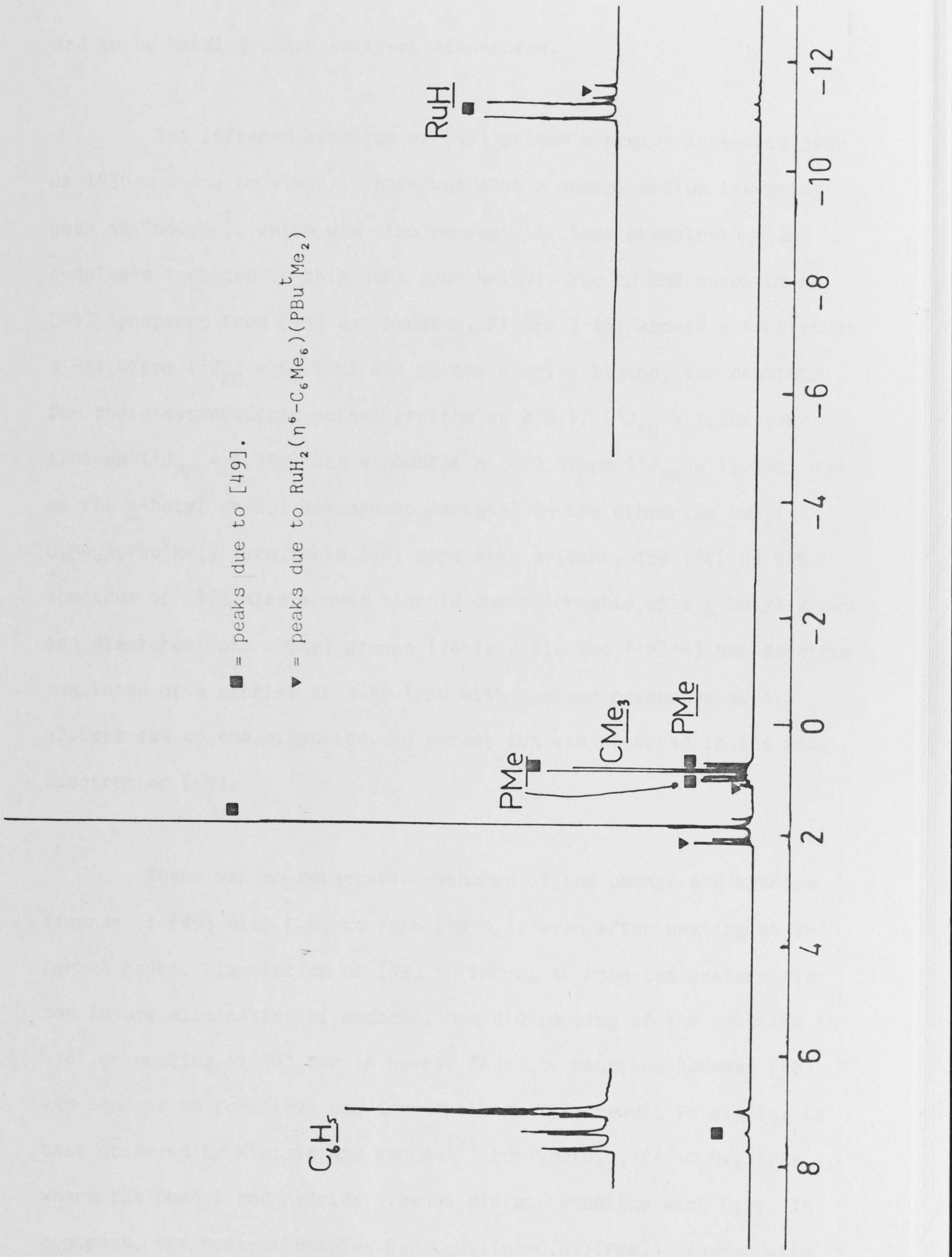


Figure 3-15: ^1H NMR spectrum of $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ [49] prepared from $RuH(CH_2CMe_2PMe_2)(\eta^6\text{-}C_6Me_6)$ [48].

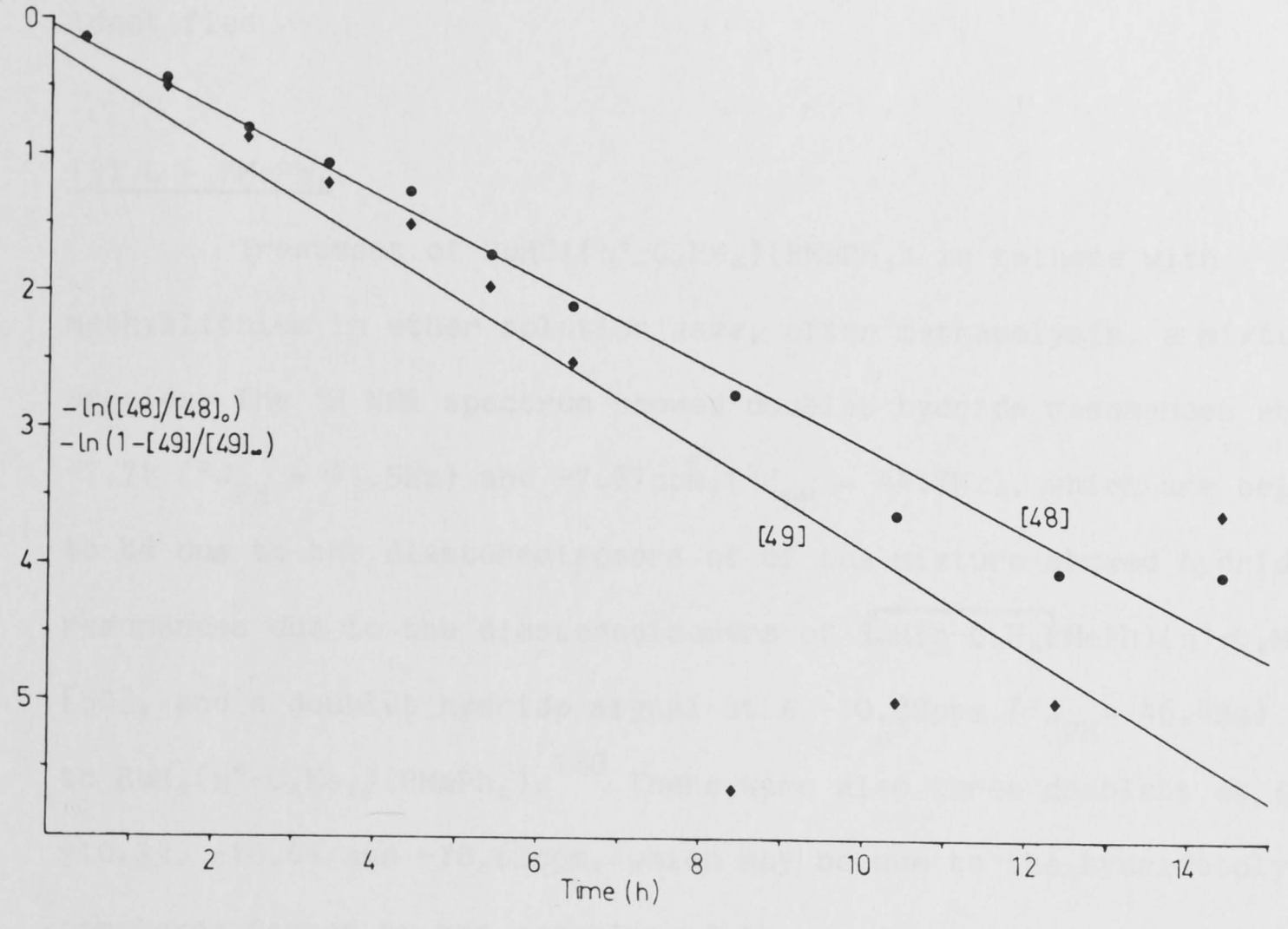
had to be handled under an inert atmosphere.

The infrared spectrum of [49] showed a medium intensity peak at 1930cm^{-1} due to ν(RuH). There was also a sharp, medium intensity peak at 1560cm^{-1}, which was also present in other phenylruthenium complexes isolated in this work {see below}. The ^{1}H NMR spectrum of [49] {prepared from [48] and benzene, Figure 3-15} showed a doublet at δ -11.07ppm ($^2J_{PH}$ = 53.7Hz) due to the hydride ligand, two doublets for the diastereotopic methyl protons at δ 0.77 ($^2J_{PH}$ = 7.9Hz) and 1.01ppm ($^2J_{PH}$ = 7.3Hz) and a doublet at δ 0.87ppm ($^2J_{PH}$ = 13.4Hz) due to the t-butyl group. Resonances assigned to the dihydride $RuH_2(\eta^6$-$C_6Me_6)(PBu^tMe_2)$ {see Table 2-4} were also evident. The $^{13}C[^1H]$ NMR spectrum of [49] also showed signals characteristic of a t-butyl group and diastereotopic methyl groups {Table 3-2}. The $^{31}P[^1H]$ NMR spectrum consisted of a singlet at δ 36.1ppm with a minor resonance at δ 42.6ppm due to the dihydride. No parent ion was observed in the mass spectrum of [49].

There was no detectable exchange of the phenyl and hydride ligands of [49] with C_6D_6 to form [49-d_6], even after heating at 70° for 24 hours. Dissolution of [49] in THF-d_8 at room temperature did not induce elimination of benzene, nor did cooling of the solution to -18° or heating at 70° for 16 hours. Thus the reaction between [48] and benzene to form [49] was irreversible. This result is similar to that observed by Kletzin and Werner[124] for $RuH(C_6H_5)(\eta^6$-$C_6Me_6)(PMe_3)$, where the phenyl and hydride ligands did not exchange with C_6D_6. In contrast, the benzene complex $RuH(C_6H_5)(\eta^6$-$C_6H_6)(PPr^i_3)$ reacted with C_6D_6 to form $RuD(C_6D_5)(\eta^6$-$C_6H_6)(PPr^i_3)$.[124]

The reaction between [48] and neat benzene {concentration: 1.7M} to form [49] was monitored at 35° by $^{31}P[^{1}H]$ NMR spectroscopy. There was apparently a very significant T_1 or NOE difference between the phosphorus resonances of [48] and [49]. However, the kinetic data were generated by following the relative rate of decay of the peak due to [48] and the relative rate of growth of the peak due to [49] using the ubiquitous dihydride as an internal reference. The reaction between [48] and benzene showed pseudo-first order kinetics {Figure 3-16}, with a rate constant of $(8.6 \pm 1.1) \times 10^{-5} s^{-1}$ {Errors quoted are 90% confidence limits}. The observed rate of formation of [49] was $(1.0 \pm 0.1) \times 10^{-4} s^{-1}$. The reaction between [48] and C_6D_6 {concentration: 0.6M} was similarly pseudo-first order {Figure 3-16}, with a rate constant of $(1.1 \pm 0.1) \times 10^{-4} s^{-1}$. The observed rate of formation of [49-d_6] was $(1.1 \pm 0.1) \times 10^{-4} s^{-1}$. While $k_H/k_D \approx 0.8$, this probably does not constitute a significant isotope effect, due to the size and nature of the experimental errors. Other experiments, for example, a reaction of [48] with a 1:1 mixture of C_6H_6 and C_6D_6, followed by preparation of derivatives and mass spectroscopic analysis of the latter, are probably necessary to ascertain any kinetic isotope effect.

The reaction of [48] with C_6D_6 to form specifically [49-d_6] containing a deuteride ligand, implies that the Ru-C bond of the cyclometallated ring must reductively eliminate with the hydride ligand to form the zero-valent ruthenium species $Ru(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$, which subsequently undergoes oxidative addition of a C-D bond in C_6D_6. In an attempt to trap this intermediate, [48] was treated with diphenylacetylene, but there was no reaction, perhaps because of steric hindrance to the approach of this bulky ligand. Treatment of [48] with methylisocyanide or t-butylisocyanide only



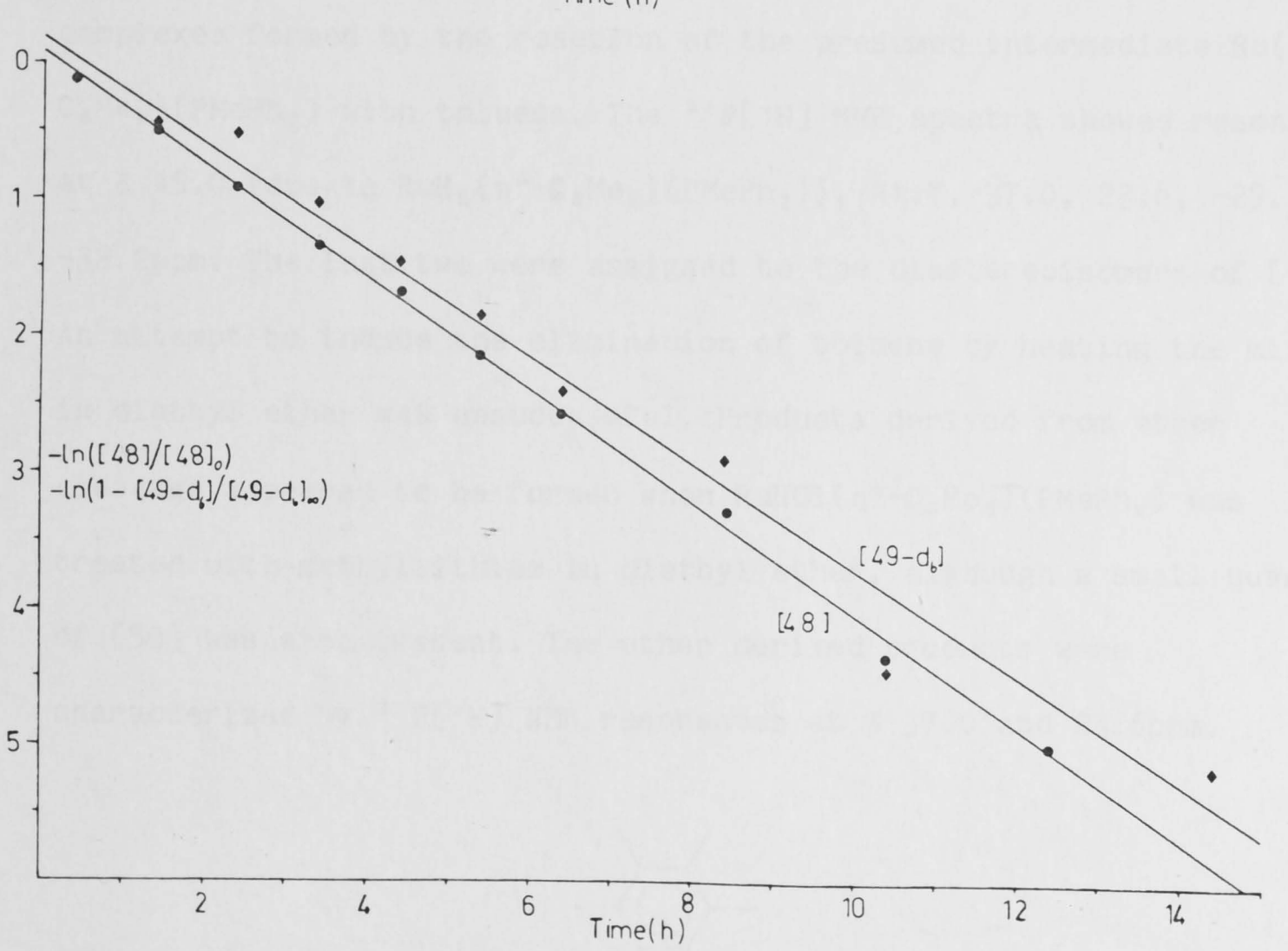
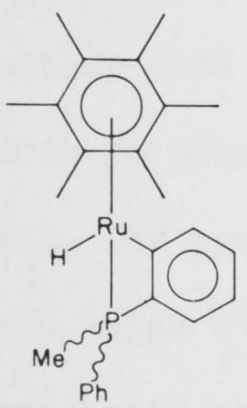


Figure 3-16: Kinetic data for the reaction between $R\overline{uH(CH_2CMe_2PMe_2)}(\eta^6\text{-}C_6Me_6)$ [48] and (i) C_6H_6, (ii) C_6D_6, including lines of best fit. For explanation of symbols, see appendix 2, p188.

caused arene displacement from [48], but the products were not identified.

13) L = $PMePh_2$

Treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PMePh_2)$ in toluene with methyllithium in ether solution gave, after methanolysis, a mixture of species. The ^1H NMR spectrum showed doublet hydride resonances at δ -7.71 ($^2J_{PH}$ = 41.5Hz) and -7.87ppm ($^2J_{PH}$ = 44.7Hz), which are believed to be due to the diastereoisomers of of the mixture showed hydride resonances due to the diastereoisomers of $\overline{RuH(\underline{o}\text{-}C_6H_4PMePh)}(\eta^6\text{-}C_6Me_6)$ [50], and a doublet hydride signal at δ -10.80ppm ($^2J_{PH}$= 46.4Hz) due to $RuH_2(\eta^6\text{-}C_6Me_6)(PMePh_2)$.[180] There were also three doublets at δ -10.34, -10.61 and -10.62ppm, which may be due to the hydridotolyl complexes formed by the reaction of the presumed intermediate $Ru(\eta^6\text{-}C_6Me_6)(PMePh_2)$ with toluene. The $^{31}P[^1H]$ NMR spectra showed resonances at δ 45.0 {due to $RuH_2(\eta^6\text{-}C_6Me_6)(PMePh_2)$}, 41.7, 37.0, 23.6, -29.7 and -32.2ppm. The last two were assigned to the diastereoisomers of [50]. An attempt to induce the elimination of toluene by heating the mixture in diethyl ether was unsuccessful. Products derived from ether cleavage appeared to be formed when $RuHCl(\eta^6\text{-}C_6Me_6)(PMePh_2)$ was treated with methyllithium in diethyl ether, although a small quantity of [50] was also present. The ether derived products were characterized by $^{31}P[^1H]$ NMR resonances at δ 37.0 and 23.6ppm.



[50] (a,b)

When n-hexane was used as the reaction medium, the product formed contained approximately 60% $RuH_2(\eta^6\text{-}C_6Me_6)(PMePh_2)$ and 40% [50], as shown by ^1H NMR spectroscopy. Attempts to separate this mixture from impurities by crystallization were unsuccessful. When TMS was used in place of n-hexane, little reaction occurred, and the only product detected was the dihydride $RuH_2(\eta^6\text{-}C_6Me_6)(PMePh_2)$.

The deprotonation of carbon atoms α to phosphorus by strong bases can give rise to cyclometallated complexes {see page 17}. An attempt was made to induce the metallation of the methyl group of the methyldiphenylphosphine ligand in $RuHCl(\eta^6\text{-}C_6Me_6)(PMePh_2)$ by treating the compound with $NaN(SiMe_3)_2$ in toluene at room temperature. The ^1H NMR spectrum of the crude product suggested that little reaction had occurred. There were two new minor hydride resonances at δ -9.03 (d, $^2J_{PH}$ = 53.7Hz) and -9.06ppm (d, $^2J_{PH}$ = 53.7Hz). There were new resonances at δ 41.2, 38.6 and 25.2ppm in the $^{31}P[^1H]$ NMR spectrum of the product. These products could not be identified, and no resonances for [50] were observed.

14) L = PMe_2Ph

The reaction between $RuHCl(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$ in benzene and freshly prepared phenyllithium gave mainly the hydridophenyl $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$ [51] and the bis(phenyl) complex $Ru(C_6H_5)_2(PMe_2Ph)$ [52]. The former could not be isolated either by sublimation or by crystallization from n-hexane at -78°. Compound [51] apparently slowly decomposed in solution, but was identified on the basis of spectroscopic results. The hydride resonance due to [51] occurred as a doublet at δ -10.49ppm ($^2J_{PH}$ = 53.7Hz) in the ^1H NMR spectrum, and the two diastereotopic methyl groups gave rise to doublets at δ 1.03 ($^2J_{PH}$ = 9.2Hz) and 1.36ppm ($^2J_{PH}$ = 8.5Hz). The peak

due to the hexamethylbenzene protons of [51] occurred at δ 1.74ppm. The phosphorus nucleus of [51] resonated at δ 24.2ppm in the $^{31}P[^{1}H]$ NMR spectrum.

The second product, $Ru(C_6H_5)_2(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$ [52], was isolated as quite air-sensitive sticky yellow crystals in low yield {ca. 5%}, but was not completely characterized. The infrared spectrum of [52] showed no peak due to ν(RuH). However, there was a strong peak at 1560cm^{-1}, which was also present in the infrared spectrum of $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ [49]. The ^1H NMR spectrum of [52] showed no hydride resonance between δ 0 and -15ppm. There was only one resonance due to the phosphine methyl protons, at δ 1.26ppm (d, $^2J_{PH}$ = 7.9Hz), which was consistent with [52] being achiral. The hexamethylbenzene protons of [52] gave rise to a sharp singlet at δ 1.54ppm, and the multiplets in the aromatic region integrated for three phenyl groups, in accord with the proposed formulation. The parent ion for [52] was present in the mass spectrum at m/z 556.

There was no evidence for intramolecular C-H bond cleavage when $RuHCl(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$ was treated with methyllithium in toluene. A ^1H NMR spectrum of the solid isolated after methanolysis and extraction with toluene showed four doublet hydride resonances of approximately equal intensity at δ -10.79ppm ($^2J_{PH}$ = 47.9Hz) due to the dihydride $RuH_2(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$, and at δ -10.48 ($^2J_{PH}$ = 53.7Hz), -10.55 ($^2J_{PH}$ = 56.2Hz), and -10.73ppm ($^2J_{PH}$ = 53.7Hz). The last three are probably due to hydridotolyl complexes formed by the reaction of the presumed intermediate $Ru(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$ with toluene.

15) L = PMe_3

Treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PMe_3)$ with methyllithium in n-hexane gave a mixture of products, of which there were two main components. One was the dihydride $RuH_2(\eta^6\text{-}C_6Me_6)(PMe_3)$, characterized by doublet resonances at δ -10.90 ($^2J_{PH}$ = 48.8Hz, Ru<u>H</u>) and 1.17ppm ($^2J_{PH}$ = 6.7Hz, P<u>Me</u>), and a singlet at δ 2.18ppm (C_6<u>Me_6</u>) in the ^{1}H NMR spectrum, and by a singlet at δ 6.7ppm in the ^{31}P[^{1}H] NMR spectrum. The other component of the mixture was apparently the dimethyl species $Ru(CH_3)_2(\eta^6\text{-}C_6Me_6)(PMe_3)$, identified by doublet resonances at δ -0.13 ($^2J_{PH}$ = 6.7Hz, Ru<u>Me</u>) and 0.97ppm ($^2J_{PH}$ = 8.5Hz, P<u>Me</u>), as well as a singlet at δ 1.74ppm (C_6<u>Me_6</u>) in the ^{1}H NMR spectrum and a singlet at δ 7.9ppm in the ^{31}P[^{1}H] NMR spectrum. Both of these complexes have been made independently by Werner and Kletzin.[180] {There was a difference in the observed values of the ^{1}H NMR chemical shifts for these compounds from those reported. The reported values of the proton chemical shifts of the dihydrides $RuH_2(\eta^6\text{-}C_6Me_6)L$[180] were 0.1 to 0.3ppm to lower field from those observed during the course of this work. The chemical shifts of $RuH_2(\eta^6\text{-}C_6Me_6)L$ were verified by preparing a sample of the dihydride independently. The observed ^{31}P chemical shifts were identical with those reported}. There were also minor resonances in the ^{1}H NMR spectrum: a small doublet at δ 0.1ppm ($J_{PH} \approx$ 7Hz), a doublet at δ 1.11ppm (J_{PH} = 7.9Hz), a singlet at δ 1.96ppm, and a very weak doublet at δ -10.81ppm (J_{PH} = 58.0Hz). These may be due to the hydridomethyl complex $RuHMe(\eta^6\text{-}C_6Me_6)(PMe_3)$. No additional ^{31}P[^{1}H] NMR resonances were observed.

When $RuHCl(\eta^6\text{-}C_6Me_6)(PMe_3)$ in benzene was treated with an excess of phenyllithium, an orange-yellow suspension formed. Methanolysis of the reaction mixture gave a reddish-purple suspension. The ^{1}H NMR spectrum of the mixture isolated after methanolysis and

extraction with benzene showed the presence of free hexamethylbenzene {δ 2.12ppm}, indicating that much decomposition had occurred. The mixture also contained the desired product, $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PMe_3)$ [53], together with a small amount of a species having ^1H NMR resonances at δ 1.61 ($C_6\underline{Me}_6$) and 0.89ppm (d, $^2J_{PH}$ = 8.5Hz, P<u>Me</u>). The latter species may have been $Ru(C_6H_5)_2(\eta^6\text{-}C_6Me_6)(PMe_3)$. Repeated attempts to crystallize [53] from the reaction mixture were unsuccessful. High vacuum sublimation gave an inhomogeneous mixture in low yield {<u>ca</u>. 8%} containing [53] and between 12% and 25% of free hexamethylbenzene. Compound [53] has been previously prepared by the photolysis of $RuH_2(\eta^6\text{-}C_6Me_6)(PMe_3)$ in benzene.[124]

The ^1H and $^{31}P[^1H]$ NMR data for [53] prepared by treatment of the chlorohydride with phenyllithium {Table 3-1} were virtually identical with those reported. The $^{13}C[^1H]$ NMR spectrum of [53] showed doublets at δ 97.3 ($^2J_{PC}$ = 3Hz, $\underline{C}_6Me_6$) and 20.9ppm ($^1J_{PC}$ = 31Hz, P<u>Me</u>), as well as singlets at δ 17.0 and 16.9ppm due to the co-ordinated and free hexamethylbenzene methyl carbon. The infrared spectrum of [53] showed a broad peak at 1940cm^{-1} due to ν(RuH). There was also a strong, sharp peak at 1560cm^{-1}. No parent ion was observed in the mass spectrum of [53].

DISCUSSION

The results of the reactions shown in Table 3-4 can be summarized as follows. Treatment of the complexes $RuHCl(\eta^6\text{-}C_6Me_6)(PR_3)$ {PR_3 = $P(\underline{p}\text{-}C_6H_4CH_3)_3$, $P(\underline{p}\text{-}C_6H_4F)_3$, PBu^tPh_2, PPh_2Pr^i, $PEtPh_2$, PPh_2Pr^n, $PPh_2\underline{o}\text{-Tol}$, PBu^t_2Me, PBu^t_2Et, $PBu^t_2Pr^n$, PPr^i_3, PBu^tMe_2, $PMePh_2$} with methyllithium generally led to cyclometallated hydrides $\overline{RuH(C\sim PR_2)}(\eta^6\text{-}C_6Me_6)$. The preferred site of cyclometallation depended

Table 3-4 : Summary of Alkylation Reactions

Result of the reaction $RuHCl(\eta^6\text{-}C_6Me_6)L$ + LiR. For specific conditions, see text.

L	LiR	Outcome (Isolated yields in parentheses) (* = not isolated)
PPh_3	LiMe	o-Metallation (58%).[14,97]
	LiPh	14:1 Mixture of o-metallation (55%) + hydridophenyl*.
$P(p\text{-}C_6H_4F)_3$	LiMe	o-Metallation (45%).
$P(p\text{-}C_6H_4CH_3)_3$	LiMe	o-Metallation (67%).
PBu^tPh_2	LiMe	Kinetic: t-butyl metallation (55%). Thermodynamic: o-metallation (41%; only one diastereoisomer isolated).
PPh_2Pr^i	LiMe	Kinetic: i-propyl methyl metallation (27%; 3:2 mixture of diastereoisomers + 13% o-metallated product). Thermodynamic: o-metallation (38%; 10:1 mixture of diastereoisomers).
$PEtPh_2$	LiMe	o-Metallation (42%; 4:1 mixture of diastereoisomers).
$PPh_2(o\text{-Tol})$	LiMe	Kinetic: 2:3 ratio of o-metallation (ca. 1:1 mixture of isomers)* + o-methyl metallation*. Thermodynamic: o-methyl metallation (25%).

Table 3-4 : Summary of Alkylation Reactions (Cont'd)

L	LiR	Outcome (Isolated yields in parentheses) (* = not isolated)
PPh_2Pr^n	LiMe	Kinetic: 1:3 mixture of propyl C-3 metallation + o-metallation (3:1 mixture of diastereoisomers) (14%). Thermodynamic: propyl C-3 metallation (47%).
	LiPh	At room temperature: 3:3:2 mixture* of o-metallation, propyl C-3 metallation and hydridophenyl.
PBu^t_2Me	LiMe	t-Butyl group metallation (42%, only one diastereoisomer observed).
PBu^t_2Et	LiMe	Kinetic: 3:2 ratio of t-butyl and ethyl C-2 metallation*. Thermodynamic: t-butyl metallation (32%; 11:1 mixture of diastereoisomers containing 10% dihydride).
$PBu^t_2Pr^n$	LiMe	Mixture of t-butyl (two diastereoisomers) and propyl C-3 metallation (57%). Equilibrium ratio 8:1:11.
PPr^i_3	LiMe	i-Propyl methyl metallation (45%; 2:1 mixture of diastereoisomers).
PBu^tMe_2	LiMe	t-Butyl metallation (35%) + dihydride (12%).
	LiPh	Hydridophenyl (12%) + hydridobromide (2%) + dihydride (0.7%).
$PMePh_2$	LiMe	3:2 ratio of dihydride* + o-metallation (3:2 mixture of diastereoisomers)*.
PMe_2Ph	LiMe	See text.
	LiPh	Hydridophenyl* + bisphenyl(5%).
PMe_3	LiMe	Mixture* of dihydride + dimethyl.
	LiPh	Hydridophenyl (8%; contaminated with free C_6Me_6).

Table 3-5 : Isomerization and Reaction Rate Constants

Species	T(°C)	Measured Rate Constants ± 90% Confidence Limit (s^{-1})	Halflife (h)	$\Delta G^{\ddagger}$ (kJ mol^{-1})
$\overline{RuH(CH_2CMe_2PPh_2)}(\eta^6\text{-}C_6Me_6)$ [31] ⟶ $\overline{RuH(\underline{o}\text{-}C_6H_4PBu^tPh)}(\eta^6\text{-}C_6Me_6)$ [32]				
[31]	50°	$(6.3 \pm 0.3) \times 10^{-5}$ (C_6D_6)	3.0	105.3
		$(5.2 \pm 0.4) \times 10^{-5}$ (THF-d_8)	3.7	105.8
[32a]*		$(5.5 \pm 0.3) \times 10^{-5}$ (C_6D_6)	3.5	105.6
		$(5.0 \pm 0.5) \times 10^{-5}$ (THF-d_8)	3.9	105.9
[32b]*		$(5.3 \pm 0.7) \times 10^{-6}$ (C_6D_6)	36	112.0
		$(5.3 \pm 1.1) \times 10^{-6}$ (THF-d_8)	36	112.0
$\overline{RuH(CH_2CHMePPh_2)}(\eta^6\text{-}C_6Me_6)$ [33] ⟶ $\overline{RuH(\underline{o}\text{-}C_6H_4PPhPr^i)}(\eta^6\text{-}C_6Me_6)$ [34] + $RuD(C_6D_5)(\eta^6\text{-}C_6Me_6)(PPh_2Pr^i)$ [35-d_6]				
[33a]*	20°	$(2.9 \pm 0.2) \times 10^{-5}$	6.7	97.3
[33b]*		$(2.6 \pm 0.2) \times 10^{-5}$	7.3	97.5
[34a]*		$(2.4 \pm 0.6) \times 10^{-5}$	8.0	97.7
[34b]*		$(2.3 \pm 0.9) \times 10^{-6}$	84	103.4
[35-d_6]		$(6. \pm 3) \times 10^{-6}$	32	101.0

Table 3-5 : Isomerization and Reaction Rate Constants (Cont'd)

Species	T(°C)	Measured Rate Constants ± 90% Confidence Limit (s^{-1})	Halflife (h)	$\Delta G^{\ddagger}$ (kJ mol^{-1})
$\overline{RuH(\underline{o}\text{-}C_6H_4PPhPr^n)}(\eta^6\text{-}C_6Me_6)$ [39] ⟶ $\overline{RuH(CH_2CH_2CH_2PPh_2)}(\eta^6\text{-}C_6Me_6)$ [40]				
[39a]*	60°	$(2.0 \pm 0.1) \times 10^{-5}$	9.6	111.9
[39b]*		$(2.1 \pm 0.2) \times 10^{-5}$	9.2	111.8
[40]		$(2.0 \pm 0.1) \times 10^{-5}$	9.5	111.8
$\overline{RuH(CH_2CMe_2PMe_2)}(\eta^6\text{-}C_6Me_6)$ [48] + C_6H_6 ⟶ $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ [49]				
[48]	35°	$(8.6 \pm 1.1) \times 10^{-5}$	2.3	99.5
[49]		$(1.0 \pm 0.1) \times 10^{-4}$	1.9	99.1
$\overline{RuH(CH_2CMe_2PMe_2)}(\eta^6\text{-}C_6Me_6)$ [48] + C_6D_6 ⟶ $RuD(C_6D_5)(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ [49-d_6]				
[48]	35°	$(1.1 \pm 0.1) \times 10^{-4}$	1.7	98.8
[49-d_6]		$(1.1 \pm 0.1) \times 10^{-4}$	1.8	99.0

* a refers to the major diastereoisomer, b refers to the minor diastereoisomer.

on the nature of the phosphine substituents. In the case of PR_3 = PMe_2Ph or PMe_3, cyclometallation was not observed. When $RuHCl(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$ was treated with toluene, $RuH_2(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$ and isomers of $RuH(tolyl)(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$ were formed. The reaction of $RuHCl(\eta^6\text{-}C_6Me_6)(PMe_3)$ with methyllithium yielded a mixture of $RuH_2(\eta^6\text{-}C_6Me_6)(PMe_3)$ and $RuMe_2(\eta^6\text{-}C_6Me_6)(PMe_3)$. The dihydrides $RuH_2(\eta^6\text{-}C_6Me_6)(PR_3)$ were by-products of the reactions of $RuHCl(\eta^6\text{-}C_6Me_6)(PR_3)$ with methyllithium when PR_3 = PBu^t_2Et, PBu^tMe_2, $PMePh_2$, PMe_2Ph and PMe_3. Treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PR_3)$ with phenyllithium gave $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PR_3)$ for small tertiary phosphine ligands {PR_3 = PMe_3, PMe_2Ph, PBu^tMe_2}, and a mixture of cyclometallated hydrides and hydridophenyls for more sterically demanding phosphines {PR_3 = PPh_3, PPh_2Pr^n}. The bis(phenyl) complex $Ru(C_6H_5)_2(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$ was a by-product of the reaction of $RuHCl(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$ with phenyllithium.

These results raise several important questions which will be addressed in this Discussion:

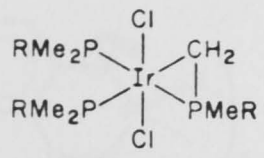
What are the factors controlling the site of cyclometallation?

What are the factors which determine whether the metallation is intramolecular or intermolecular?

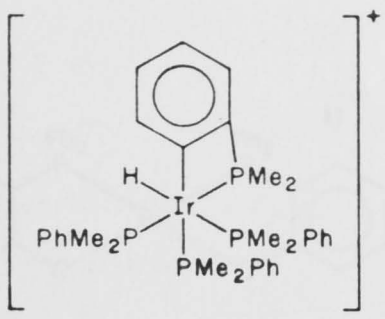
What is the mechanism of the reaction between $RuHCl(\eta^6\text{-}C_6Me_6)L$ and organolithium reagents?

How are the dihydrido and dimethyl or bis(phenyl) by-products formed?

During the discussion of the first two questions, it will be assumed that the reaction of $RuHCl(\eta^6\text{-}C_6Me_6)(PR_3)$ with organolithium reagents to give the cyclometallated products proceeds via oxidative addition of a substituent C-H bond in the intermediate $Ru(\eta^6\text{-}C_6Me_6)(PR_3)$. The



[21] {R = Ph}

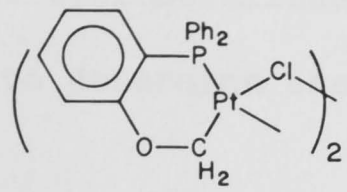


[15]

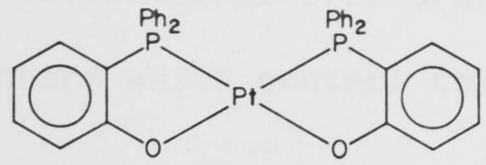
discussion of the last two questions will analyse this assumption.

1) Cyclometallation reactions

Previously, cyclometallation at two different sites of a tertiary phosphine has been observed only in a few instances, and there appears to have been no demonstration of an isomerization from one site of metallation to another. Dimethylphenylphosphine, when co-ordinated to iridium, can be metallated at either the methyl group or an ortho-position of the phenyl ring. Treatment of mer-$IrCl_3(PMe_2Ph)_3$ with $LiNPr^i_2$, $LiBu^n$ or $Li(CH_2)_5Li$ gave $IrCl_2(CH_2PMePh)(PMe_2Ph)_2$ [21].[3] In contrast, when $[IrCl(COD)]_2$ was heated for a long time with PMe_2Ph, an aryl C-H bond oxidatively added to iridium(I) to form fac-$[IrH(o\text{-}C_6H_4PMe_2)(PMe_2Ph)_3]^+$ [15], probably via the intermediate $[Ir(PMe_2Ph)_4]^+$.[57] When $[IrCl(cyclooctene)_2]_2$ was heated with $PBu^t_2Pr^n$ or $PBu^t_2Bu^n$ in the presence of γ-picoline or acetonitrile, a mixture of products was obtained in which metallation had occurred either at C-3 of the n-alkyl group or in the t-butyl group.[88] Metallation of the methoxy carbon atom to form $[Pt(o\text{-}CH_2OC_6H_4PPh_2)(\mu\text{-}Cl)]_2$ [54] was observed when $PPh_2(o\text{-}C_6H_4OMe)$ was heated with $PtCl_2(NCPh)_2$ in xylene, whereas $PtCl_2[PPh_2(o\text{-}C_6H_4OMe)]_2$ eliminated chloromethane to yield the O-bonded chelate complex $Pt(o\text{-}OC_6H_4PPh_2)_2$ [55] on heating in 2-methoxyethanol.[109]



[54]



[55]

In tertiary phosphine complexes, H-D exchange is believed to proceed via cyclometallated intermediates. The complex $Pt_2Cl_4(PBu^tPh_2)_2$ underwent H-D exchange in D_2O/CH_3CO_2D at both the ortho sites of phenyl groups and in the t-butyl group, phenyl H-D exchange being fifty times faster than for the t-butyl group. However, in the corresponding PPh_2Pr^n and $PPhPr^n_2$ complexes, exchange occurred exclusively at the terminal methyl groups. The analogous $PBu^t_2Pr^n$ complex showed rapid exchange at the C-3 position of the propyl moiety, with slower exchange at the C-2 position and in the t-butyl methyl groups.[117] In contrast, H-D exchange with D_2 gas in all the alkyl as well as the ortho-phenyl sites of PPh_2Pr^n was catalysed by $RuHCl(PPh_3)_3$ in benzene. The rate of H-D exchange depended on the site, the order being as follows: ortho, C-3 > C-1 > C-2. Under the same conditions, H-D exchange in the ortho position of the phenoxy group was fifty times faster than in the ortho site of the phenyl groups in $PPh_2(OPh)$.[121] The results for H-D exchange in PBu^tPh_2 and $PBu^t_2Pr^n$ do not agree well with the relative rates found for cyclometallation of $Ru(\eta^6\text{-}C_6Me_6)L$: the oxidative addition of the t-butyl group to the arene ruthenium fragment was much more rapid than a phenyl group when L = PBu^tPh_2, and was competitive with metallation of the n-propyl terminal carbon when L = $PBu^t_2Pr^n$.

The arene ruthenium compounds derived from $Ru(\eta^6\text{-}C_6Me_6)(PR_3)$ appear to be the first class of complexes which yield both kinetic and thermodynamic cyclometallated products. This offers an unprecedented opportunity to determine the factors which control their formation.

The thermodynamically preferred products obtained from the cyclometallation of $Ru(\eta^6\text{-}C_6Me_6)(PPh_2R)$ {R = Et, Pr^i, Pr^n, Bu^t, o-Tol} were those which would have been expected from trends reported in the literature for the metallation of non-symmetrically substituted phosphines[46,47,136,188] {see also ref. 144}. The relative thermodynamic stabilities of the complexes lead to the following stability order: four-membered alkyl rings < four-membered aryl rings < five-membered rings. However, the initial product distribution does not reflect the thermodynamic stability of the products.

The isomerization of the kinetic products formed from $Ru(\eta^6\text{-}C_6Me_6)(PR_3)$ implies that the metallation reaction is reversible, and must proceed by reductive elimination of a C-H bond to form the fragment $Ru(\eta^6\text{-}C_6Me_6)(PR_3)$. There are several pieces of evidence which support this assertion:

1) The first-order kinetic behaviour observed for the isomerization reactions of $\overbrace{RuH(CH_2CMe_2PPh_2)}(\eta^6\text{-}C_6Me_6)$ [31], $\overbrace{RuH(CH_2CHMePPh_2)}(\eta^6\text{-}C_6Me_6)$ [33] and $\overbrace{RuH(o\text{-}C_6H_4PPhPr^n)}(\eta^6\text{-}C_6Me_6)$ [39], which implies that these reactions are probably intramolecular.

2) The reaction of $\overbrace{RuH(CH_2CMe_2PMe_2)}(\eta^6\text{-}C_6Me_6)$ [48] with C_6D_6 to form specifically $RuD(C_6D_5)(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ [49].

3) The competitive formation of $RuD(C_6D_5)(\eta^6\text{-}C_6Me_6)(PPh_2Pr^n)$ [41-d_6] during the isomerization of $\overbrace{RuH(o\text{-}C_6H_4PPhPr^n)}(\eta^6\text{-}C_6Me_6)$ [39] to $\overbrace{RuH(CH_2CH_2CH_2PPh_2)}(\eta^6\text{-}C_6Me_6)$ [40] in C_6D_6.

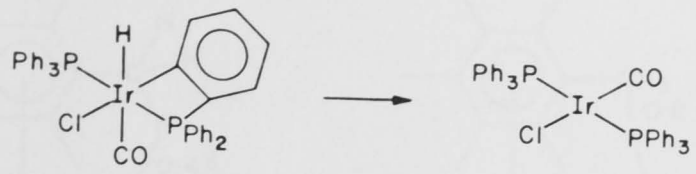


Figure 3-17

The reductive elimination of a cyclometallated phosphine hydride has precedent. The complex $\overline{IrHCl(o\text{-}C_6H_4PPh_2)}(CO)(PPh_3)$ spontaneously reductively eliminates the metallated phenyl group to form $IrCl(CO)(PPh_3)_2$[172] {Figure 3-17}. The reactions of $\overline{IrHCl(o\text{-}C_6H_4PPh_2)}(PPh_3)_2$ [16] with D_2, DCl and Cl_2 suggest that it can revert to its iridium(I) precursor, $IrCl(PPh_3)_3$.[20] Similarly, $\overline{RuH(o\text{-}C_6H_4PPh_2)}(CO)(PPh_3)_2$ behaves as $Ru(CO)(PPh_3)_3$ in its reactions with H_2, HCl and CO.[154] The complex $Ru(\eta^6\text{-}C_6H_6)(PPr^i_3)$ is believed to be an intermediate in the reaction of $\overline{RuH(CH_2CHMePPr^i_2)}(\eta^6\text{-}C_6H_6)$ with benzene to form $RuH(C_6H_5)(\eta^6\text{-}C_6H_6)(PPr^i_3)$.[124]

2) Factors Controlling the Site of Cyclometallation

There are a number of important factors which apparently control the site of cyclometallation:

1) Steric effects;

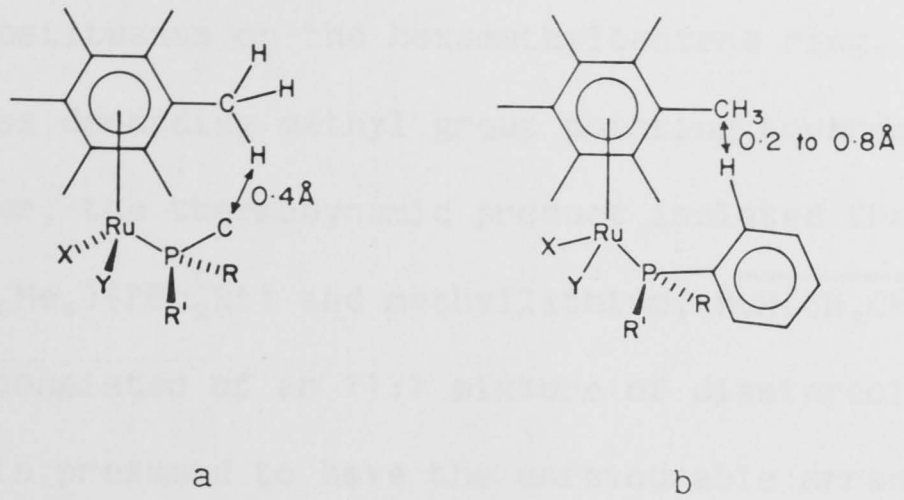
2) Ruthenium-carbon bond strengths;

3) Ring strain.

It is the balance achieved between these factors which determines the outcome of the cyclometallation reactions.

2.1 Steric Effects

The system $Ru(\eta^6\text{-}C_6Me_6)(PR_3)$ is sterically relatively



a b

Figure 3-18

hindered. Assuming co-planarity of the intermediate atoms, and standard values for bond angles and lengths {ie: d(C-H) = 1.09A, d(C-C) = 1.54A, d(C-C) = 1.39A [benzene], d(Ru-P) = 2.34A, d(P-C) = 1.82A, d(Ru-$C_{\eta^6\text{-arene}}$) = 2.22A}, the nuclei of a hexamethylbenzene proton and the α-carbon of a phosphine ligand substituent would be about 0.4A apart {Figure 3-18a}. The assumption of co-planarity is clearly unreasonable. However, Huang[97] estimated from models that the distance between the ortho-hydrogen atom of an arylphosphine and a methyl hydrogen atom on hexamethylbenzene could be in the range 0.2 to 0.8A {Figure 3-18b}. The crowded nature of hexamethylbenzene ruthenium complexes is also suggested by the dissociation of the phosphine ligand from $RuCl_2(\eta^6\text{-}C_6Me_6)(PBu^tPh_2)$ in solution, and the failure to prepare $RuCl_2(\eta^6\text{-}C_6Me_6)L$ when L is sterically very demanding {eg: L = PCy_3, PBu^t_2R}.

The cyclometallation reactions of $Ru(\eta^6\text{-}C_6Me_6)(PR_2R')$ often gave rise to diastereoisomers. The difference in the size of the substituents R and R' influenced the stereoselectivity of the cyclometallations. The fact that $RuH(CH_2CMe_2PBu^tMe)(\eta^6\text{-}C_6Me_6)$ [42], which was formed from $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2)$ and methyllithium, exists as only one diastereoisomer illustrates this point clearly. The

proposed structure of [42] has the t-butyl group pointing away from the methyl substituents on the hexamethylbenzene ring, and the sterically less demanding methyl group pointing towards the arene ligand. However, the thermodynamic product isolated from the reaction of $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$ and methyllithium, $\overline{RuH(CH_2CMe_2}PBu^tEt)(\eta^6\text{-}C_6Me_6)$ [43], consisted of an 11:1 mixture of diastereoisomers. The minor isomer is presumed to have the unfavourable arrangement in which the t-butyl group points towards the arene ligand. Although an ethyl group is less sterically demanding than a t-butyl group, it is sterically more demanding than a methyl group, so the energy difference between the diastereoisomers is now presumably smaller than it was in the case of PBu^t_2Me. The diastereoselectivity of the cyclometallation of $PMePh_2$ was low; a ratio of isomers of 3:2 was observed. The range of selectivity observed fell between the two extremes of PBu^t_2Me and $PMePh_2$.

Shaw[160] has explained the tendency of bulky substituents to promote cyclometallation by noting that they restrict rotation, and hence a sterically crowded molecule is intrinsically low in rotational entropy. Cyclization in such a situation would not result in a large drop in entropy, whereas cyclometallation in an uncrowded environment is entropically much less favourable. He also suggested an enthalpy effect: formation of rings bearing geminal substituents would introduce fewer additional gauche interactions than in the unsubstituted case. This effect was first suggested by Allinger and Zalkow[4] in their discussion of the hypothetical formation of cyclohexanes from various substituted hexanes. Small rings may also be stabilized by bulky gem-substituents, as these will tend to cause a decrease in the angle between the other two substituents on the central atom; this is called the Thorpe-Ingold effect {Figure 3-19}.[11]

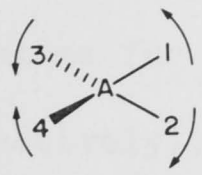


Figure 3-19

The cyclometallation reactions of $Ru(\eta^6\text{-}C_6Me_6)(PPh_2R")$ {R" = Bu^t, Pr^i, Et} are consistent with the scheme shown in Figure 3-20. Since $\overline{Ru(CH_2CMe_2PPh_2)}(\eta^6\text{-}C_6Me_6)$ [31] was formed exclusively at low temperature, $k_1 >> k_2$ for R" = Bu^t. In the case of R" = Pr^i, $\overline{RuH(CH_2CHMePPh_2)}(\eta^6\text{-}C_6Me_6)$ [33] could not be prepared free from $\overline{RuH(\underline{o}\text{-}C_6H_4PPhPr^i)}(\eta^6\text{-}C_6Me_6)$ [34]. This probably is because k_{-1} is much larger than in the case of R" = Bu^t, and because k_1 and k_2 are of comparable magnitude at low temperature. No ethyl metallated complex was observed for R" = Et; thus $k_2 \geqq k_1$ and k_{-1} is large in this case. The results from the metallation of PBu^t_2Et in $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$ show that ethyl group metallation can occur, although it is not as favourable a process as phenyl or t-butyl group

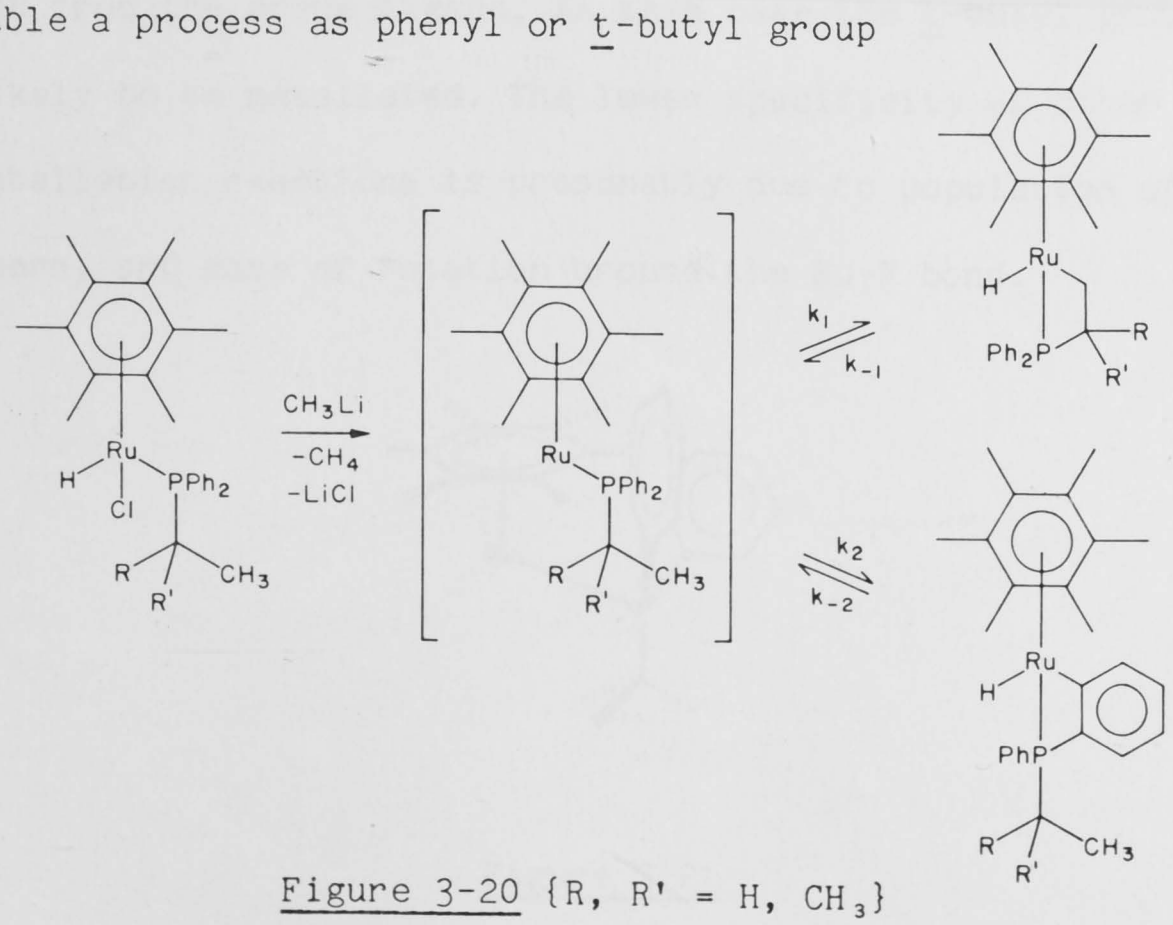


Figure 3-20 {R, R' = H, CH_3}

metallation. For the cyclometallated derivatives of $Ru(\eta^6\text{-}C_6Me_6)(PPh_2R")$ {R" = Bu^t, Pr^i, Et}, k_{-2} is probably not significant. The large difference in $\Delta G^{\ddagger}$ values for the isomerization of [31] and [33] {105 and 97kJ mol^{-1} respectively}, and the fact that the ease of formation of the alkyl metallated kinetic products follows the order R = Bu^t > Pr^i > Et, suggests that steric factors are involved. Statistical factors may also be operating; there are many more t-butyl protons than ortho-aryl protons, while there are fewer terminal ethyl protons.

The ground state configuration of $Ru(\eta^6\text{-}C_6Me_6)(PR_3)$ is probably bent, by analogy with the prediction based on extended Hückel calculations for the electronically similar fragments $M(\eta^5\text{-}C_5H_5)(PR_3)$ {M = Rh, Ir}.[93] A study of models suggests that the most likely conformation of $Ru(\eta^6\text{-}C_6Me_6)(PBu^tPh_2)$ is that shown in Figure 3-21. At low temperature, rotation about the Ru-P bond is likely to be restricted. A plausible explanation for the specificity of the reaction of $Ru(\eta^6\text{-}C_6Me_6)(PBu^tPh_2)$ to give $\overline{RuH(CH_2CMe_2PPh_2)}(\eta^6\text{-}C_6Me_6)$ [31] at low temperature is therefore, that the phosphine substituent furthest from the arene ligand, in this case the t-butyl group, is the most likely to be metallated. The lower specificity of other cyclometallation reactions is presumably due to population of other conformers, and ease of rotation around the Ru-P bond.

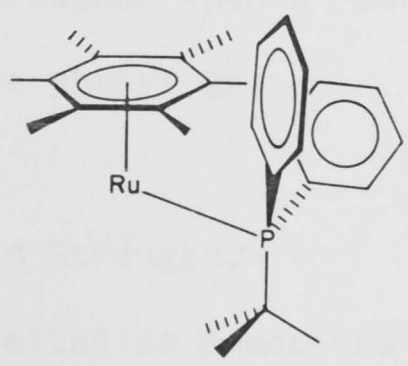


Figure 3-21

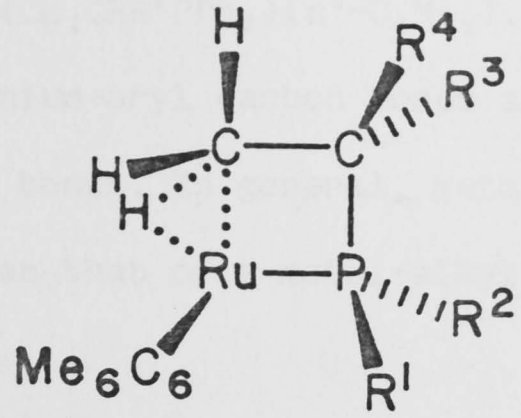


Figure 3-22

The transition state for the cyclometallation of a t-butyl group probably contains a hydrogen atom bridging the ruthenium and metallated carbon atoms {Figure 3-22, R^3,R^4 = Me}. Agostic interactions, three-centre two-electron $\overline{C\text{-}H\text{-}M}$ bonds, were suggested to be models for such transition states,[52] as was discussed briefly on page 17. Consideration of this transition state suggests several factors which help to stabilize the metallated form: 1) an unfavourable gauche interaction between the bridging hydrogen atom and R^3; 2) for the reductive elimination to proceed, R^3 and R^4 have to move closer to R^1 and R^2, which is an unfavourable situation if R^1 and R^2 are bulky. This explains the stability of the kinetic products formed by cyclometallation of $Ru(\eta^6\text{-}C_6Me_6)(PPh_2R")$ {R" = Bu^t, Pr^i, Et}, namely that as R^3 and R^4 become smaller, the activation barrier to reductive elimination decreases. Similarly, ethyl group metallation was observed for PBu^t_2Et but not for PPh_2Et, since the barrier to reductive elimination is higher when R^1 and R^2 are bulky t-butyl groups than when they are phenyl groups.

2.2 Ruthenium-Carbon Bond Strength.

In the cyclometallation reactions of $Ru(\eta^6\text{-}C_6Me_6)(PPh_2R")$ {R" = Bu^t, Pr^i, Et}, the aryl-metallated complexes $\overline{RuH(o\text{-}C_6H_4PPhR")}(\eta^6\text{-}C_6Me_6)$ were thermodynamically preferred over the alkyl

metallated isomers $\overline{RuH(CH_2CRR'PPh_2)}(\eta^6\text{-}C_6Me_6)$. This preference is probably because ruthenium-aryl carbon bonds are stronger than ruthenium-alkyl carbon bonds. In general, metal-aryl carbon bond strength is greater than that of a metal-alkyl carbon bond.[37,164]

The activation barrier to the reductive elimination of an ortho-metallated hydrido complex is significantly higher than that of analogous four-membered ring alkyl metallated complexes. The activation barrier estimated for the isomerization of $\overline{RuH(o\text{-}C_6H_4PPhPr^n)}(\eta^6\text{-}C_6Me_6)$ [39] was 112kJ mol^{-1}, while the isomerization of $\overline{RuH(CH_2CMe_2PPh_2)}(\eta^6\text{-}C_6Me_6)$ [31] had an activation barrier of 105kJ mol^{-1}. In some cases, there were barely detectable traces of the isomers of $\overline{RuH(o\text{-}C_6H_4PPh\{o\text{-}Tol\})}(\eta^6\text{-}C_6Me_6)$ [37] present even after heating the mixture of [37] and $\overline{RuH(o\text{-}CH_2C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$ [38] at 70° for fourteen hours. Both of these observations can be accounted for by ruthenium-aryl carbon bonds being stronger than ruthenium-alkyl carbon bonds.

2.3 Ring Strain.

The degree of ring strain in phosphorus containing metallacycles decreases in the order three-membered rings > four-membered rings > five-membered rings; five-membered metallacycles have relatively little strain.[144] The thermodynamic products formed by the cyclometallation of $Ru(\eta^6\text{-}C_6Me_6)(PPh_2R)$ {R = Pr^n, o-Tol} were five-membered ring complexes $\overline{RuH(CH_2CH_2CH_2PPh_2)}(\eta^6\text{-}C_6Me_6)$ [40] and $\overline{RuH(o\text{-}CH_2C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$ [38]. Severe strain in three-membered rings is probably the reason why no metallation of phosphorus methyl substituents in $Ru(\eta^6\text{-}C_6Me_6)(PMeRR')$ was observed.

Whilst steric effects are obviously important in controlling the site of cyclometallation, it is the balance of the three factors discussed above which determines the outcome of the cyclometallation reactions. This is clearly illustrated by the cyclometallation of $PBu^{t}_{2}Pr^{n}$. The thermodynamic product obtained by treatment of $RuHCl(\eta^{6}\text{-}C_{6}Me_{6})(PBu^{t}_{2}Pr^{n})$ with methyllithium was an approximately 1:1 mixture of the t-butyl and n-propyl metallated complexes respectively. In this case, the relief of steric hindrance achieved by metallation of a t-butyl group is almost balanced by the low ring strain inherent in forming a five-membered ring.

3) Factors Controlling Intramolecular and Intermolecular Metallation Reactions

The factors controlling the intramolecular or intermolecular selectivity of these reactions are those mentioned in the previous section, namely, steric effects, ruthenium-carbon bond strengths and ring strain. There is a gradation in behaviour of $Ru(\eta^{6}\text{-}C_{6}Me_{6})(PR_{3})$ which reflects the balance of the three factors controlling the selectivity of these reactions.

Very bulky tertiary phosphine ligands cause exclusive cyclometallation. The thermodynamic advantages derived from cyclometallation in a sterically very demanding environment far outweigh the possible effects of ring strain and favourable formation of a ruthenium-aryl carbon bond.

The deuteridoaryls $RuD(C_{6}D_{5})(\eta^{6}\text{-}C_{6}Me_{6})L$ {$L = PPh_{2}Pr^{i}$, $PPh_{2}Pr^{n}$} were formed competitively in the isomerization of $\overline{RuH(CH_{2}CHMePPh_{2})}(\eta^{6}\text{-}C_{6}Me_{6})$ [33] and $\overline{RuH(\underline{o}\text{-}C_{6}H_{4}PPhPr^{n})}(\eta^{6}\text{-}C_{6}Me_{6})$ [39] in $C_{6}D_{6}$. Treatment of $RuHCl(\eta^{6}\text{-}C_{6}Me_{6})(PPh_{2}Me)$ with methyllithium in

toluene gave a mixture of cyclometallated and hydridotolyl complexes. A mixture of the hydridoaryl $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PPh_3)$ [28] and the ortho-metallated species $\overline{RuH(o\text{-}C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$ [27] was formed by the reaction of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ with phenyllithium. Thus, cyclometallation and external aryl C-H bond scission are competitive for sterically less demanding phosphines such as PPh_3, PPh_2Pr^i, PPh_2Pr^n and PPh_2Me. For these intermediate ligands, the steric factors favouring cyclometallation almost balance the lack of ring strain and favourable ruthenium-aryl bond energy arising from benzene C-H bond cleavage.

The formation of hydridotolyl species on treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$ with methyllithium, and the stability of $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PMe_3)$ show that selective intermolecular bond cleavage occurs for sterically undemanding ligands such as PMe_3 and PMe_2Ph. Clearly ring strain and strong ruthenium-aryl bonds are the predominant effects in complexes bearing these ligands.

The behaviour of $Ru(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ occupies an apparently unique position in this scheme. Kinetically, cyclometallation to form $\overline{RuH(CH_2CMe_2PMe_2)}(\eta^6\text{-}C_6Me_6)$ [48] and reaction with toluene to form the hydridotolyl complexes $RuH(tolyl)(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ are competitive, but the thermodynamically favoured products are aryl hydrides such as $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ [49]. The reaction of [48] with benzene yielding [49] was first order in complex, with an estimated activation barrier of 99kJ mol^{-1}, which is of a similar magnitude to those of the isomerization reactions of the cyclometallated complexes {97 to 112kJ mol^{-1}}. Compound [49] did not exchange aryl and hydride ligands with C_6D_6, which is in accord with the behaviour reported by Kletzin and Werner[124] for $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PMe_3)$ [53]. In contrast,

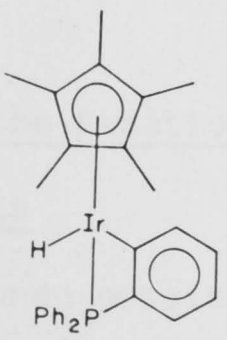
however, they reported that the benzene complex $RuH(C_6H_5)(\eta^6\text{-}C_6H_6)(PPr^i_3)$ [10] exchanged aryl and hydride ligands with C_6D_6. More data are required before the factors influencing the lability of the hydride and phenyl ligands in these complexes can be elucidated.

In this work, no evidence was found for attack on aliphatic solvents by $Ru(\eta^6\text{-}C_6Me_6)L$. Kletzin and Werner[124] reported a similar result: no reaction was observed on photolysis of $RuH_2(\eta^6\text{-}C_6Me_6)(PMe_3)$ in cyclohexane. This observation does not directly show that cyclohexane does not oxidatively add to $Ru(\eta^6\text{-}C_6Me_6)(PMe_3)$, because a hydridocyclohexyl complex could have been formed by oxidative addition of cyclohexane, and this could have subsequently decomposed by β-elimination of cyclohexene to regenerate the dihydride. Nevertheless, this explanation is unlikely to be correct. Both the iridium and rhodium n-propyl complexes $MH(C_3H_7)(\eta^5\text{-}C_5Me_5)(PMe_3)$, and the iridium cycloalkyl analogues, were reported to be stable towards β-elimination.[105,111]

There may be several reasons for the paucity of ruthenium hydridoalkyl complexes. One possibility is that alkyl ruthenium-carbon bond strengths in $RuHR(\eta^6\text{-}C_6Me_6)L$ are probably not sufficiently great to overcome the tendency for cyclometallation or other reactions, such as the formation of dialkyls and dihydrides. Treatment of $RuHCl(\eta^6\text{-}C_6Me_6)L$ with methyllithium may not be a suitable means of generating the hydridoalkyl complexes, since this reaction proceeds readily only above -20°, and the compounds $RuHR(\eta^6\text{-}C_6Me_6)L$ may be too labile under these conditions. However, no firm conclusions can be drawn at this stage.

4) A Comparison of the Fragments $Ru(\eta^6\text{-}C_6Me_6)L$, $Ir(\eta^5\text{-}C_5Me_5)L$ and $Rh(\eta^5\text{-}C_5Me_5)L$

The co-ordinatively unsaturated intermediates $Ru(\eta^6\text{-}C_6Me_6)(PR_3)$, $Ir(\eta^5\text{-}C_5Me_5)(PR_3)$ and $Rh(\eta^5\text{-}C_5Me_5)(PR_3)$ are all capable of cleaving intramolecular and intermolecular C-H bonds. However, there are some important differences in the reactivity of these species. The rhodium complex $RhH(C_6H_5)(\eta^5\text{-}C_5Me_5)(PMe_3)$ readily exchanges the phenyl and hydride ligands with C_6D_6 at 60°,[111] whereas $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PMe_3)$[124] and $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ [49] do not. The rhodium hydridoalkyl adducts $RhHR(\eta^5\text{-}C_5Me_5)(PMe_3)$ decompose above -20°,[111] but the iridium compounds $IrHR(\eta^5\text{-}C_5Me_5)(PMe_3)$ {R = pentyl, cyclohexyl} do not exchange alkyl and hydride ligands with free alkanes below 110°.[177] Thus it is likely that $IrH(C_6H_5)(\eta^5\text{-}C_5Me_5)(PMe_3)$ would be very resistant to exchange of phenyl and hydride ligands with C_6D_6. Irradiation of $IrH_2(\eta^5\text{-}C_5Me_5)(PPh_3)$ in benzene gave a 1:1 mixture of the ortho-metallated complex [56] and hydridophenyl complex [57]. Thus, intramolecular and intermolecular aryl C-H bond scission are equally favourable processes for $Ir(\eta^5\text{-}C_5Me_5)(PPh_3)$,[105] but the oxidative addition of external C-H bonds is much less favourable for $Ru(\eta^6\text{-}C_6Me_6)(PPh_3)$. Thus the stability of the hydridoaryl species increases in the order $RhH(C_6H_5)(\eta^5\text{-}C_5Me_5)L$ < $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)L$ < $IrH(C_6H_5)(\eta^5\text{-}C_5Me_5)L$.



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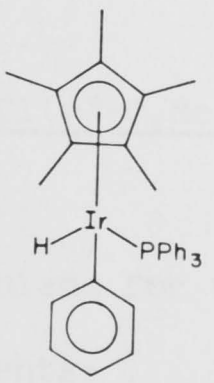


[57]

Electronic effects probably contribute to the pattern of reactivity observed. It has been implied that the activity of the iridium systems towards C-H bonds follows the electron-rich nature of the metal atom in the series $Ir(\eta^5\text{-}C_5Me_5)(PR_3)$ > $Ir(\eta^5\text{-}C_5Me_5)(CO)$ > $Ir(\eta^5\text{-}C_5H_5)(CO)$.[96] Where $Ru(\eta^6\text{-}C_6Me_6)(PR_3)$ and $Rh(\eta^5\text{-}C_5Me_5)(PR_3)$ fit into this series is not clear. However, the difference between alkyl and aryl carbon-metal bond strengths is apparently much less for iridium and rhodium than for ruthenium.

It has recently been reported that $Re(\eta^5\text{-}C_5H_5)(PMe_3)_2$ will oxidatively add the C-H bonds of benzene, cyclopropane, ethylene and a range of alkanes, whereas $Re(\eta^5\text{-}C_5Me_5)(PMe_3)_2$ will only add benzene, cyclopropane or methane C-H bonds.[25] This result is not consistent with the electronic effects noted above, but may be due to steric effects. Steric effects may also contribute to the apparent inactivity of the areneruthenium fragments $Ru(\eta^6\text{-}C_6Me_6)(PR_3)$ towards alkane C-H bonds. Hexamethylbenzene is a more sterically demanding ligand than pentamethylcyclopentadienyl. The cone angles of the fragments $Rh^I(\eta^5\text{-}C_5Me_5)$ and $Ru^0(\eta^6\text{-}C_6Me_6)$ have been estimated to be 182° and 192° respectively.[134] The importance of steric effects on the thermodynamic stability of $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)L$ has already been noted. However, a proper assessment of the factors determining the stability of the hydridoalkyls $RuHR(\eta^6\text{-arene})L$ requires further appropriately designed experiments.

5) The Mechanism of the Reaction of $RuHCl(\eta^6\text{-}C_6Me_6)L$ with Organolithium Reagents

There are three possible mechanisms for the reaction between $RuHCl(\eta^6\text{-}C_6Me_6)L$ and organolithium reagents:

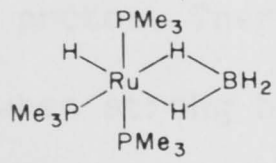
1) Substitution of Cl^- by R^- to form a hydridophenyl or

hydridomethyl species. The latter subsequently can undergo reductive elimination of RH to form Ru(η^6-C_6Me_6)L which then cyclometallates.

2) Deprotonation of a tertiary phosphine substituent, and subsequent substitution of Cl^- by the carbanion to form a cyclometallated species.

3) Abstraction of the hydride ligand as a proton and subsequent elimination of the chloride ion to form Ru(η^6-C_6Me_6)L. The latter then cyclometallates.

The reaction between RuHCl(η^6-C_6Me_6)L and methyllithium is believed to proceed via the ruthenium hydridomethyl complex RuHMe(η^6-C_6Me_6)L {for example, Figure 3-1}, although this complex has not been observed directly. The fact that $\overline{Ru(\underline{o}\text{-}C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$ [27] is formed, even though in low yield, from $RuMe(O_2CCF_3)(\eta^6\text{-}C_6Me_6)(PPh_3)$ and sodium borohydride supports this view. The second product in this reaction, from which [27] could not be separated, has not been characterized, but spectroscopic evidence indicates that it contains a borohydride group attached to the Ru(η^6-C_6Me_6)(PPh_3) moiety. Various borohydride complexes of ruthenium are known. The X-ray crystal structure of mer-RuH(η^2-BH_4)(PMe_3)$_3$ [58] was published recently.[166] Ruthenium complexes containing η^1-borohydrido[94] and η^2-borohydrido[26,56,127] ligands have been described.



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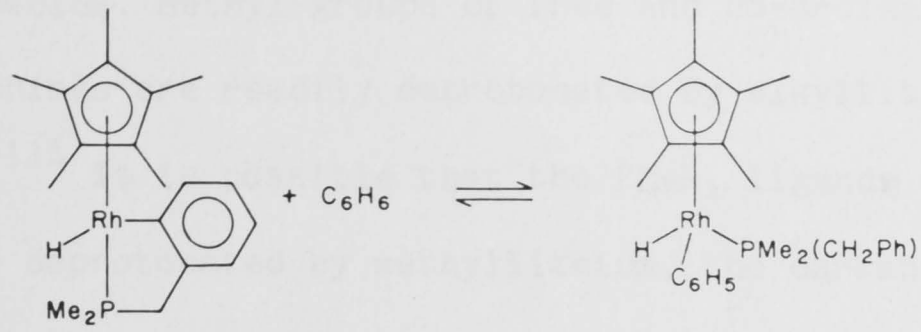


Figure 3-23

Further support for the formation of hydridoalkyl species in the cyclometallation reactions is the presence of the hydridophenyl $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PPh_3)$ [28] in the reaction mixture formed by treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$ with phenyllithium. While [28] appears to be stable at room temperature, and hence may be considered a by-product, the equilibrium established between $\overline{RuH(CH_2CH_2CH_2PPh_2)}(\eta^6\text{-}C_6Me_6)$ [40] and $RuD(C_6D_5)(\eta^6\text{-}C_6Me_6)(PPh_2Pr^n)$ [41-d_6] in C_6D_6 demonstrates that the elimination of benzene from hydridophenyl complexes is a viable route to the cyclometallated complexes. Recently, a similar equilibrium was observed between the pairs of pentamethylcyclopentadienylrhodium compounds $\overline{RhH(\underline{o}\text{-}C_6H_4CH_2PMe_2)}(\eta^5\text{-}C_5Me_5)$ and $RhH(C_6H_5)(\eta^5\text{-}C_5Me_5)(PMe_2[CH_2Ph])$ {Figure 3-23}, and $\overline{RhH(CH_2CH_2CH_2PMe_2)}(\eta^5\text{-}C_5Me_5)$ and $RhH(C_6H_5)(\eta^5\text{-}C_5Me_5)(PMe_2Pr^n)$, respectively, with benzene.[112]

The cyclometallation reaction proceeds via an oxidative addition reaction at an unsaturated metal centre rather than by base abstraction of a phosphine proton. There was very little cyclometallation observed when strong bases such as $KOBu^t$ and $NaN(SiMe_3)_2$ were added to $RuHCl(\eta^6\text{-}C_6Me_6)L$. Furthermore, when organolithium reagents reacted with the adducts $RuHCl(\eta^6\text{-}C_6Me_6)L$ {L = PBu^tMe_2, PBu^t_2Me, $PMePh_2$}, there was no evidence for the formation of

$\overline{RuCH_2PR_2}$ species. Methyl groups of free and co-ordinated methylphosphines are readily deprotonated by alkyllithium reagents.[3,116] It is possible that the $PMeR_2$ ligands of $RuHCl(\eta^6\text{-}C_6Me_6)L$ are deprotonated by methyllithium, the carbanion then displacing the chloro ligand to form a hydridometallacycle $\overline{RuH(CH_2PR_2)}(\eta^6\text{-}C_6Me_6)$. This could undergo rapid reductive elimination of the phosphine methyl group to form the unsaturated species $Ru(\eta^6\text{-}C_6Me_6)L$; the latter would then cyclometallate. However, the compounds $RuHCl(\eta^6\text{-}C_6Me_6)L$ {L = PBu^tMe_2, PMe_2Ph, PMe_3} form stable hydridophenyl complexes when treated with phenyllithium. To propose different pathways for reactions with methyllithium or phenyllithium when there is no evidence to support these propositions is clearly unjustified.

Another alternative is that the intermediate $Ru(\eta^6\text{-}C_6Me_6)L$ is generated by abstraction of the hydride ligand as a proton by the organolithium reagent, with subsequent loss of chloride ion. The abstraction of hydride ligands by base has been observed in a number of instances.[66,82,158,163] The complex $\overline{RuH(CH_2CMe_2PMe_2)}(\eta^6\text{-}C_6Me_6)$ [48] was a product of the reaction between $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ and phenyllithium in diethyl ether. Compound [48] cannot arise from $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ [49] as the latter is stable with respect to reductive elimination of benzene. Thus, in diethyl ether, phenyllithium may be abstracting the hydride ligand from $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$. Treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ with methyllithium in toluene gave a mixture of [48] and hydridotolyl species. However, when $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ was treated with phenyllithium in benzene, no [48] was observed. This clearly militates against the proton abstraction pathway in benzene, as formation of [48] from $Ru(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ is competitive with aryl C-H bond scission, and its lifetime in aromatic solvents {$t_{1/2} \approx 2h$ in benzene

at 35°} should have enabled [48] to be detected if it had been formed.

6) Formation of the Dihydrido and Dialkyl By-Products

The reaction of $RuHCl(\eta^6\text{-}C_6Me_6)L$ with alkyllithium reagents probably proceeds via hydridoalkyl species and $Ru(\eta^6\text{-}C_6Me_6)L$. However, this simple picture does not account for the formation of the dialkyl and dihydrido by-products in a number of these reactions, particularly those in which L is a small phosphine. The frequent appearance of the dihydrido complexes suggests that they are formed very readily in these reactions. The work-up procedure was not responsible for the formation of the dihydrides, because there was no detectable deuterium incorporation in $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ formed from $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ and methyllithium after methanolysis with CD_3OD. There are four possible explanations for the formation of the dihydrido complexes.

6.1 β-Elimination of Alkene from Intermediate Hydridoalkyls

Treatment of $RuHCl(\eta^6\text{-}C_6Me_6)L$ with methyllithium generates the species $Ru(\eta^6\text{-}C_6Me_6)L$. When L is a small tertiary phosphine, the latter may oxidatively add a C-H bond from the alkane solvent, forming a hydridoalkyl. The hydridoalkyl complexes might be unstable with respect to β-elimination, decomposing by a pathway similar to that shown in Figure 3-24 {X = CH_2}. However, when $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ was treated with methyllithium in tetramethylsilane, $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ was still formed. Since a (trimethylsilyl)methyl intermediate would have no β-proton, the explanation cannot hold in this case. It has already been noted in Section 3 of this Discussion that analogous iridium and rhodium hydridoalkyls were stable with respect to β-elimination.[105,111] Thus this explanation seems improbable.

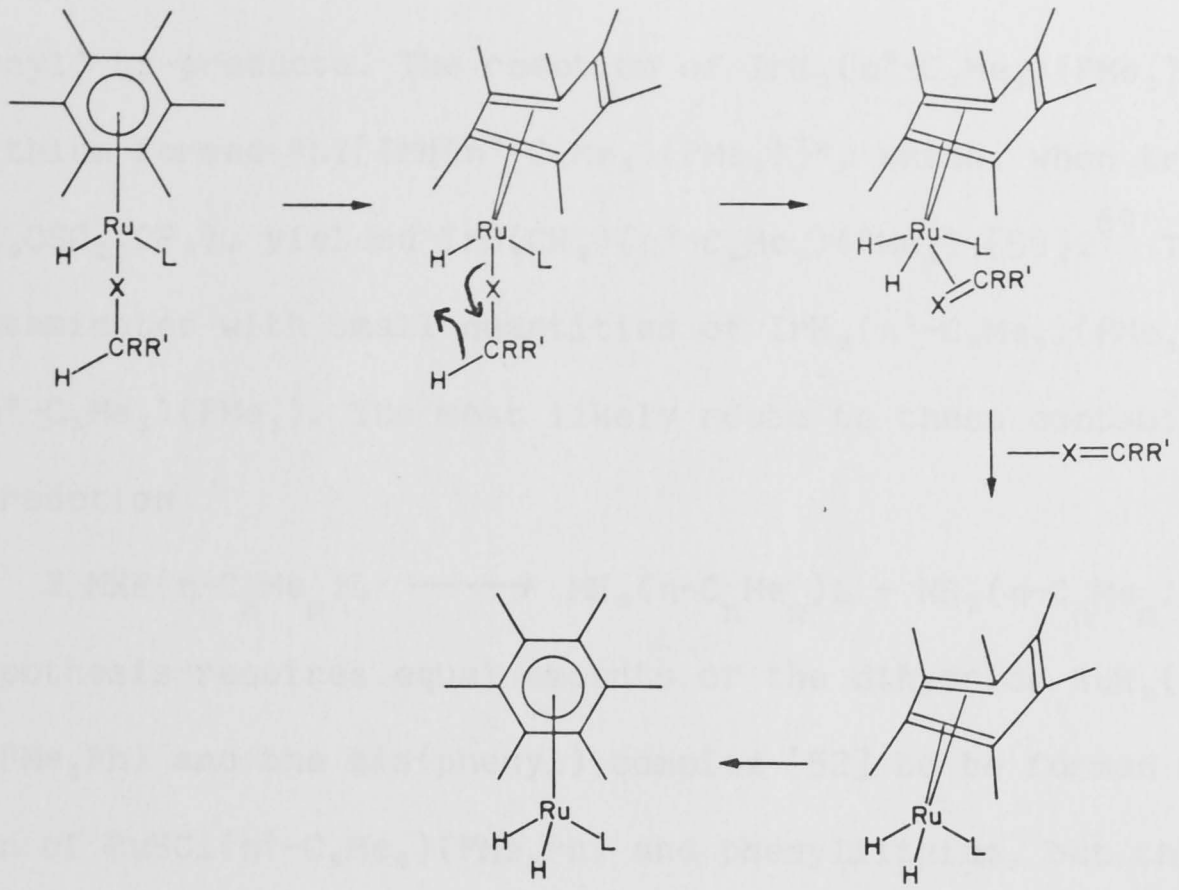


Figure 3-24 {X = CH_2, O}

6.2 α-Elimination Reactions

Another possible explanation for the formation of the dihydrides from $RuHCl(\eta^6\text{-}C_6Me_6)L$ and methyllithium is by "α-elimination", or a 1,2-hydrogen shift,[79] that is, transfer of a hydrogen atom from a methyl ligand to ruthenium, forming a ruthenium hydridomethylidene complex such as $RuH_2(CH_2)(\eta^4\text{-}C_6Me_6)L$ or $RuH_2(CH_2)(\eta^6\text{-}C_6Me_6)$. The intermediate $[WH(CH_2)(\eta^5\text{-}C_5H_5)_2]^+$ is believed to be involved in the reaction between $[WMe(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}C_2H_4)]^+$ and tertiary phosphines to form $[WH(CH_2PR_3)(\eta^5\text{-}C_5H_5)_2]^+$.[41,51] Dissociation of tertiary phosphine ligands from hydridoruthenium complexes, or an η^6- to η^4-arene shift in ruthenium(II) complexes, are unlikely. Furthermore, α-elimination has only been clearly demonstrated for early transition metal complexes.Thus this explanation is also improbable.

6.3 Disproportionation or Redistribution Reactions

Disproportionation or redistribution reactions could account for the simultaneous formation of the dihydrido and dimethyl or

bis(phenyl) by-products. The reaction of $IrH_2(\eta^5\text{-}C_5Me_5)(PMe_3)$ with t-butyllithium formed "$Li[IrH(\eta^5\text{-}C_5Me_5)(PMe_3)]$", which, when treated with $CH_3OSO_2(CF_3)$, yielded $IrH(CH_3)(\eta^5\text{-}C_5Me_5)(PMe_3)$ [59].[69] The latter was contaminated with small quantities of $IrH_2(\eta^5\text{-}C_5Me_5)(PMe_3)$ and $IrMe_2(\eta^5\text{-}C_5Me_5)(PMe_3)$. The most likely route to these contaminants is by the reaction

$$2\ MHR(\eta\text{-}C_nMe_n)L \longrightarrow MH_2(\eta\text{-}C_nMe_n)L + MR_2(\eta\text{-}C_nMe_n)L.$$

This hypothesis requires equal amounts of the dihydride $RuH_2(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$ and the bis(phenyl) complex [52] to be formed from the reaction of $RuHCl(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$ and phenyllithium, but this was not observed.

Organolithium species are oligomeric species. The reaction of $RuHCl(\eta^6\text{-}C_6Me_6)L$ with organolithium reagents probably proceeds by interaction of the organolithium oligomers with the ruthenium complexes. In fact, stable polynuclear aggregates of transition metal complexes with lithium alkyls have been isolated.[50,108] An alternative explanation to disproportionation is that when the oligomeric organolithium reagents interact with $RuHCl(\eta^6\text{-}C_6Me_6)L$, redistribution of chloro, hydrido and alkyl groups may occur, to give the observed products. However, the displacement of a hydride ligand {as opposed to the abstraction of a hydride ligand as a proton} by an organolithium reagent is an unusual reaction, and this is not an entirely satisfactory explanation.

6.4 Pathways Involving Lithium Alkoxides

It has been known for a long time that lithium reagents cleave diethyl ether forming lithium ethoxide;[191] for example, in twelve days at 35°, phenyllithium in diethyl ether was found to have halved in concentration,[73] although methyllithium was much more

stable. Traces of moisture and oxygen also result in alkoxide formation in organolithium solutions.[72] Lithium alkoxides might react with $RuHCl(\eta^6\text{-}C_6Me_6)L$ to form alkoxo complexes, which subsequently could undergo β-elimination as illustrated in Figure 3-24 {X = O}. Lithium methoxide and lithium ethoxide alone did not react with $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$, which may be due to the insolubility of lithium salts in hexane. However, lithium reagents are oligomeric species, and recent NMR studies of butyllithium in THF have demonstrated that mixed oligomers of butyllithium and lithium butoxide were present.[132] The interaction of organolithium/lithium alkoxide oligomers with $RuHCl(\eta^6\text{-}C_6Me_6)L$ may represent an efficient means of bringing alkoxides close to the metal. Transfer of an alkyl group would result in a hydridoalkyl, which would then react further. However, transfer of an alkoxide will form an alkoxo adduct, which could then undergo β-elimination of an aldehyde to form the observed dihydride.

Interaction with lithium alkoxides may alter the reactivity of alkyllithium reagents. It has been reported that the addition of alkali metal alkoxides enhanced the reactivity of sodium hydride/metal salt reducing reagents[36] and the basicity of sodium amide in THF.[42] For example, butyllithium alone did not metallate diphenyl-ortho-tolylphosphine, but mixtures of butyllithium and potassium or sodium t-butoxide gave the potassium and sodium alkyls $o\text{-}MCH_2C_6H_4PPh_2$;[129] lithium t-butoxide in combination with butyllithium was found to be ineffective. The authors thought that the most likely explanation for these results was that transmetallation yielded the very reactive n-butylsodium or n-butylpotassium.

$$MOBu^t + LiBu^n \longrightarrow LiOBu^t + MBu^n$$

It is not obvious how the presence of lithium alkoxides in

organolithium reagents will alter the reactivity of the latter to form dihydrido or dialkyl complexes from $RuHCl(\eta^6\text{-}C_6Me_6)(PR_3)$ when PR_3 is small.

The source of the dihydride and dialkyl complexes is not certain. Several of the above mentioned pathways may be operating. It might be possible to shed some light on this problem by studying the reaction of $RuHCl(\eta^6\text{-}C_6Me_6)L$ with methyllithium free of alkoxides, or with CD_3Li.

CONCLUSIONS

The reactions of $RuHCl(\eta^6\text{-}C_6Me_6)(PR_3)$ with methyllithium lead to the cyclometallated products $\overbrace{RuH(C\text{-}PR_2)}(\eta^6\text{-}C_6Me_6)$ except when PR_3 = PMe_3, PMe_2Ph. In many of these reactions, the dihydrides are formed as by-products. In phosphine complexes with two possible sites of cyclometallation, the thermodynamic stability of the products is determined by the nature of the chelate ring formed. The thermodynamic stabilities of the rings are in the order four-membered alkyl ring < four-membered aryl ring < five-membered ring. However, the initial product distribution does not reflect the thermodynamic stability of the products. The stability of the kinetic products formed by metallation of PPh_2R follows the order R = Bu^t > Pr^i > Et. For the phosphines PPh_2o-Tol, PPh_2Pr^n, PBu^t_2Et and $PBu^t_2Pr^n$, there is competition between the sites of metallation, although for the latter three, careful control of the reaction conditions can enhance the proportion of the kinetic product. In no case is the formation of a three-membered ring observed, and no attack at C-2 of the propyl group is observed for L = $PBu^t_2Pr^n$. The results for L = PPh_2Pr^n are not as

conclusive, although attack at C-2 is not very favourable. In the case of the metallation of $PBu^{t}_{2}Pr^{n}$, isomers formed by metallation of a t-butyl group and an n-propyl group exist in an approximate 1:1 ratio at equilibrium.

In cases where cyclometallation gives rise to diastereoisomers, that isomer with the less bulky substituent pointing towards the hexamethylbenzene ring is probably favoured.

The isomerization of the kinetic products from cyclometallation reactions is first order and proceeds by reductive elimination of the metallated group. The rate of isomerization of the kinetic product is dependent on the nature of the metallated group. The reductive elimination of a metallated aryl group is slower than that of a metallated t-butyl group, which is in turn slower than that of a metallated isopropyl group. The reaction of $\overline{RuH(CH_2CMe_2PMe_2)}(\eta^6\text{-}C_6Me_6)$ [48] with neat benzene to give $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PBu^{t}Me_2)$ [49] is pseudo-first order and irreversible. These reactions probably proceed via the sixteen electron intermediates $Ru(\eta^6\text{-}C_6Me_6)(PR_3)$, and demonstrate that internal oxidative addition of alkyl and aryl C-H bonds of phosphine substituents in $Ru(\eta^6\text{-}C_6Me_6)(PR_3)$ is reversible.

Treatment of the hydrido complexes $RuHCl(\eta^6\text{-}C_6Me_6)(PR_3)$ with methyllithium probably forms the hydridomethyl complexes $RuH(CH_3)(\eta^6\text{-}C_6Me_6)(PR_3)$, though these have not been directly observed. These then reductively eliminate methane to give the sixteen electron fragment, $Ru(\eta^6\text{-}C_6Me_6)(PR_3)$, the further reactions of which depend on the tertiary phosphine present.

Treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PR_3)$ {PR_3 = PBu^tMe_2, $PMePh_2$} with methyllithium in aromatic solvents generates a species, presumably $Ru(\eta^6\text{-}C_6Me_6)(PR_3)$, which undergoes competitive intramolecular and intermolecular attack on C-H bonds. Further, the attack on C-H bonds for PR_3 ligands smaller than these is exclusively intermolecular, whereas for PR_3 ligands larger than PPh_2Me, it is preferentially intramolecular, becoming exclusively intramolecular for very bulky phosphines. Thus the factor determining whether C-H bond cleavage is intramolecular or intermolecular is the nature of the tertiary phosphine ligand. There was no evidence for attack on aliphatic solvents.

Many of the products from the alkylation reactions contain varying quantities of the dihydrides $RuH_2(\eta^6\text{-}C_6Me_6)L$. It has not been possible to determine the origin of the dihydrides, although these may arise from alkoxides present in organolithium reagents, but the matter has not been settled. Other possibilities, for example, α-elimination and disproportionation of the intermediate hydridomethyl complex, have been considered, but do not seem very likely.

The site of C-H bond scission by $Ru(\eta^6\text{-}C_6Me_6)(PR_3)$ is determined by a balance of steric effects, ruthenium-carbon bond strengths and ring strain.

EXPERIMENTAL

Methyllithium {ca. 1 to 2M in diethyl ether, lithium oxide and lithium alkoxides usually ca. 0.3M} obtained from EGA-Chemie was used throughout these experiments. Phenyllithium {ca. 1M in diethyl ether} was prepared by literature methods.[74] Alkyllithium reagents were standardized prior to use[71] and were stored in sealed Schlenk tubes at ca. 4°C. n-Hexane, when used as a reaction medium, was distilled from sodium benzophenone ketyl/tetraglyme prior to use. When used to recrystallize compounds, it was not predried. Methanol was not predried unless specified, when it was distilled from calcium hydride. For further procedural details, see the experimental section of Chapter 2.

The preparation of the compounds $\overline{RuH([\underline{o}\text{-}C_6H_3\text{-}\underline{p}\text{-}F]P[\underline{p}\text{-}C_6H_4F]_2)}(\eta^6\text{-}C_6Me_6)$ [29], $\overline{RuH([\underline{o}\text{-}C_6H_3\text{-}\underline{p}\text{-}CH_3]P[\underline{p}\text{-}C_6H_4CH_3]_2)}(\eta^6\text{-}C_6Me_6)$ [30], $\overline{RuH(\underline{o}\text{-}CH_2C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$ [38], $\overline{RuH(\underline{o}\text{-}C_6H_4PPhPr^i)}(\eta^6\text{-}C_6Me_6)$ [34][97] and $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PMe_3)$ [53][124] have been previously described, but they were prepared by different methods.

1) Preparation of $\overline{RuH([o\text{-}C_6H_3\text{-}p\text{-}F]P[p\text{-}C_6H_4F]_2)}(\eta^6\text{-}C_6Me_6)$ [29]

A suspension of $RuHCl(\eta^6\text{-}C_6Me_6)(P[\underline{p}\text{-}C_6H_4F]_3)$ (0.39g , 0.63mmol) in toluene (10ml) was cooled to -78°. Methyllithium (1.5M, 2.0ml, 3.0mmol) was added dropwise. The suspension was allowed to warm to room temperature and was stirred at room temperature for 50 min. The suspension dissolved to give a pale yellow solution, which then slowly darkened to red. The red solution was cooled to -78°, and methanol (0.5ml) added dropwise. The pale yellow solution was permitted to warm to room temperature and was evaporated to dryness under reduced pressure. The residue was extracted with toluene, the

extract reduced in volume and n-hexane added, forming [29] as a fine yellow powder (0.17g, 0.29mmol , 45%).

The following were prepared in an analogous fashion (yields in parentheses): $Ru\overline{H([\underline{o}\text{-}C_6H_3\text{-}\underline{p}\text{-}CH_3]P[\underline{p}\text{-}C_6H_4CH_3]_2)}(\eta^6\text{-}C_6Me_6)$ [30] (67%); $Ru\overline{H(\underline{o}\text{-}C_6H_4PEtPh)}(\eta^6\text{-}C_6Me_6)$ [36] (42%).

$Ru\overline{H(CH_2CHMePPr^i_2)}(\eta^6\text{-}C_6Me_6)$ [47] was prepared similarly from $RuHCl(\eta^6\text{-}C_6Me_6)(PPr^i_3)$, but after removal of the solvent, the residue was extracted with toluene. The extract was evaporated to dryness, and recrystallized from n-hexane by cooling to -78°, yielding golden clusters of microcrystals of [47] in 45% yield.

The complexes $Ru\overline{H(CH_2CMe_2PBu^tMe)}(\eta^6\text{-}C_6Me_6)$ [42] and $Ru\overline{H(CH_2CMe_2PBu^tEt)}(\eta^6\text{-}C_6Me_6)$ [43] {the latter containing 10% $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$} were prepared from $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Me)$ and $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$ in a similar manner to [29], but the reaction mixtures were stirred at room temperature for 2h and 4h respectively. After methanolysis and removal of the solvent, the residue was extracted with toluene, and the toluene extract was evaporated to dryness under reduced pressure leaving brown solids. Sublimation of the residues at $110°/10^{-5}$mm Hg onto a cold finger at -20° gave [42] (42% yield) and [43] (32% yield) as very pale yellow powders.

Similar treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Pr^n)$ with methyllithium gave a mixture of $Ru\overline{H(CH_2CMe_2PBu^tPr^n)}(\eta^6\text{-}C_6Me_6)$ [45] and $Ru\overline{H(CH_2CH_2CH_2PBu^t_2)}(\eta^6\text{-}C_6Me_6)$ [46] in 57% yield after sublimation under vacuum.

Treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2\underline{o}\text{-}Tol)$ with methyllithium, following the synthetic method for [29], gave a mixture of $\overline{Ru\underline{H}(\underline{o}\text{-}CH_2C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$ [38] and $\overline{Ru\underline{H}(\underline{o}\text{-}C_6H_4PPh[\underline{o}\text{-}Tol])}(\eta^6\text{-}C_6Me_6)$ [37] in the approximate ratio 60:40. The mixture was studied spectroscopically but was not isolated.

Attempts to prepare $\overline{Ru\underline{H}(\underline{o}\text{-}C_6H_4AsPh_2)}(\eta^6\text{-}C_6Me_6)$ and $\overline{Ru\underline{H}(\underline{o}\text{-}C_6H_4SbPh_2)}(\eta^6\text{-}C_6Me_6)$ by this method were unsuccessful. Treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(AsPh_3)$ with a twofold excess of methyllithium in toluene at -78°, followed by stirring at room temperature for fifty minutes, methanolysis at 78° and recrystallization from toluene/n-hexane gave two crops of grey solids whose infrared spectra were almost identical with that of triphenylarsine. The ^1H NMR spectrum of the third crop suggested that this contained mainly $RuHCl(\eta^6\text{-}C_6Me_6)(AsPh_3)$. The filtrate decomposed on further handling.

Similar treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(SbPh_3)$ with a fourfold excess of methyllithium yielded only several crops of dark intractable solids. An NMR spectrum of the filtrate showed that this was a complex mixture containing neither the starting material nor the desired product.

2) Preparation of $\overline{Ru\underline{H}(o\text{-}C_6H_4PBu^tPh)}(\eta^6\text{-}C_6Me_6)$ [32]

A suspension of $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tPh_2)$ (0.52g, 0.96mmol) in toluene (10ml) was cooled to -78°. Methyllithium (1.5M, 2.6ml, 3.9mmol) was added dropwise to the suspension, and this was allowed to warm to room temperature. The suspension was heated in an oil bath at 70° for four hours, during which time it rapidly faded to a pale yellow solution, and then slowly darkened to black. The black solution

was cooled to -78° and methanol (2ml) was added dropwise. The resultant yellow suspension was allowed to warm to room temperature, and was evaporated to dryness under reduced pressure. The residue was extracted with toluene. The toluene extract was reduced in volume, and n-hexane was added, yielding fine yellow crystals of [32] (0.20g , 0.39mmol, 41%).

$Ru\overline{H(\underline{o}\text{-}C_6H_4PPhPr^i)}(\eta^6\text{-}C_6Me_6)$ [34] was prepared similarly from $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2Pr^i)$ in 38% yield.

$Ru\overline{H(\underline{o}\text{-}CH_2C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$ [38] was prepared by treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2\underline{o}\text{-}Tol)$ in toluene with a fivefold excess of methyllithium at -78° and stirring at room temperature for one hour. The brown solution was methanolyzed at -78°, evaporated to dryness under reduced pressure and the residue was extracted with toluene. The toluene extract was heated at 70° for 14h and the solution was cooled and evaporated to dryness. Recrystallization from toluene/n-hexane gave [38] as tan crystals in 25% yield.

The synthesis of $Ru\overline{H(CH_2CH_2CH_2PPh_2)}(\eta^6\text{-}C_6Me_6)$ [40] from $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2Pr^n)$ was similar to that of [38]. After methanolysis, the solution was evaporated under reduced pressure and the residue was extracted with n-hexane. The hexane extract was heated to reflux for 14h. The yellow-brown suspension was cooled and evaporated to dryness under reduced pressure. Recrystallization from toluene/n-hexane gave [40] as fine golden crystals in 47% yield.

3) Preparation of $\overline{RuH(CH_2CMe_2PPh_2)}(\eta^6\text{-}C_6Me_6)$ [31]

A suspension of $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tPh_2)$ (0.32g, 0.59mmol) in diethyl ether (10ml) was cooled to -78° and treated dropwise with methyllithium (1.6M, 1.0ml, 1.6mmol). The yellow suspension was stirred in an ice bath for 3h, and was then cooled to -78° and treated dropwise with methanol (1.0ml). The solution was evaporated to dryness under reduced pressure at 0°. The residue was extracted with cold toluene, and the extract was evaporated to dryness under reduced pressure at 0°. The pale yellow solid was recrystallized from THF/n-hexane by cooling to -78°, yielding [31] as an off-white powder (0.17g, 0.33mmol, 55%).

The compound $\overline{RuH(CH_2CHMePPh_2)}(\eta^6\text{-}C_6Me_6)$ [33] was prepared analogously from $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2Pr^i)$, except that the temperature was maintained at -18° by use of a jacketed Schlenk tube connected to a cooling bath. After methanolysis at -18°, the suspension was evaporated to dryness at -18°. The residue was extracted with cold toluene and was evaporated to dryness under reduced pressure as rapidly as possible by warming the flask with a cold water bath. The residue was recrystallized from THF/n-hexane by cooling to -78°, giving [33] as a fine pale yellow powder in 27% yield {containing 13% of $\overline{RuH(\underline{o}\text{-}C_6H_4PPhPr^i)}(\eta^6\text{-}C_6Me_6)$ [34]}.

Similarly, $\overline{RuH(\underline{o}\text{-}C_6H_4PPhPr^n)}(\eta^6\text{-}C_6Me_6)$ [39] was prepared by treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2Pr^n)$ with an excess of methyllithium in a jacketed Schlenk tube connected to a cooling bath at -20°. After methanolysis at -20°, the yellow suspension was evaporated to dryness under reduced pressure. The residue was extracted with toluene and the toluene extract was evaporated to dryness as rapidly as possible, the flask being warmed in a cold water bath. The resulting yellow solid

was extracted with diethyl ether, and the ether extract was reduced in volume to 5ml. A slight orange precipitate formed on standing, and this was filtered off. The filtrate was reduced in volume, and was allowed to stand at -78° overnight, forming fine yellow crystals of [39]. A second crop of [39] was collected and washed with n-hexane (1ml). The filtrate was discarded. The total yield of product was 14%; it contained 25% of [40].

$RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$ (0.38g, 0.80mmol) was treated similarly with methyllithium at -20° for 3h, then was allowed to warm to -10° for 3h. Methanolysis, evaporation to dryness, and extraction with n-hexane (2x20ml, 1x10ml) at -20° gave a brown solution. Evaporation of the solution to 5ml and cooling overnight at -78° gave 6mg of a light brown powder which was found to be unreacted $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$. The filtrate was evaporated to dryness under reduced pressure, yielding a brown powder (75mg) which contained $\overline{RuH(CH_2CMe_2PBu^tEt)}(\eta^6\text{-}C_6Me_6)$ [43] (75%), $\overline{RuH(CH_2CH_2PBu^t_2)}(\eta^6\text{-}C_6Me_6)$ [44] (15%), and $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^t_2Et)$ (10%), as estimated by ^1H NMR spectroscopy.

Attempts to prepare $\overline{RuH(CH_2CH_2PPh_2)}(\eta^6\text{-}C_6Me_6)$ from $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2Et)$ by this method gave only $\overline{RuH(\underline{o}\text{-}C_6H_4PEtPh)}(\eta^6\text{-}C_6Me_6)$ [36].

Treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2\underline{o}\text{-Tol})$ with methyllithium at low temperature gave a mixture consisting mainly of $\overline{RuH(\underline{o}\text{-}CH_2C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$ [38], together with some $\overline{RuH(\underline{o}\text{-}C_6H_4PPh[\underline{o}\text{-Tol}])}(\eta^6\text{-}C_6Me_6)$ [37].

4) Preparation of $\overline{RuH(CH_2CMe_2PMe_2)}(\eta^6\text{-}C_6Me_6)$ [48]

Methyllithium (1.0M, 2.4ml, 2.4mmol) was evaporated to dryness under reduced pressure, and the residue was dried in vacuo for two minutes. $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ (0.42g, 1.0mmol) was added and the reaction vessel was cooled to -78°. n-Hexane (10ml) was added slowly, the suspension was allowed to warm to room temperature and was stirred at room temperature for 3.5h. The suspension rapidly turned dark green, and then slowly turned yellow-brown. The suspension was cooled to -78° and dry methanol (0.5ml) was added dropwise. The black solution was allowed to warm to room temperature and was evaporated to dryness under reduced pressure. The residue was extracted with n-hexane, and the hexane extract was evaporated to dryness under reduced pressure, leaving a brown oil. Sublimation of the brown oil at $100°/10^{-5}$mm Hg onto a cold finger at -20° gave a yellow-green powder. Sublimation of the yellow-green powder yielded an extremely air-sensitive pale yellow glassy solid (0.10 g) containing the product $\overline{RuH(CH_2CMe_2PMe_2)}(\eta^6\text{-}C_6Me_6)$ [48] (0.19mmol, 19%) and $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ (0.081mmol, 8%). The product typically contains 25 - 30% $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ when prepared in this manner.

Similar treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PMePh_2)$ with methyllithium gave a yellow-brown solid which contained $RuH_2(\eta^6\text{-}C_6Me_6)(PMePh_2)$ (60%) and $\overline{RuH(\underline{o}\text{-}C_6H_4PMePh)}(\eta^6\text{-}C_6Me_6)$ [50] (40%), as estimated by ^{1}H NMR spectroscopy. Attempts to separate this mixture from impurities were unsuccessful.

5) Preparation of $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ [49]

A) From $\overline{RuH(CH_2CMe_2PMe_2)}(\eta^6\text{-}C_6Me_6)$ [48] generated *in situ* and benzene.

Methyllithium (2.0M, 3.0ml, 6.0mmol) was evaporated to dryness under reduced pressure, and the residue was dried *in vacuo* for two minutes. $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ (0.51g, 1.23mmol) was added and the reaction vessel was cooled to -78°. n-Hexane (10ml) was added slowly and the reaction mixture was stirred at room temperature for 5h, during which the suspension rapidly turned dark green, and then slowly turned orange. The suspension was cooled to -78° and methanol (0.5ml) was added dropwise. The suspension was allowed to warm to room temperature and was evaporated to dryness under reduced pressure. The residue was extracted with n-hexane (30ml) and the extract was evaporated to dryness, forming a yellow solid. The yellow solid was dissolved in benzene and was heated at 40 to 45° for 15h. The yellow solution was evaporated to dryness under reduced pressure. Sublimation of the residue at 95°/3×10^{-6}mm Hg, onto a cold finger at -20° gave a yellow-green solid. The yellow-green solid was purified by sublimation, yielding a bright yellow oil (0.16 g) which solidified on standing. This was a mixture of $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ [49] (0.33mmol, 27%) and $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ (2.5μmol, 2%), as estimated by ^{1}H NMR spectroscopy.

B) From $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ and phenyllithium.

Phenyllithium (0.84M, 5.0ml, 4.2mmol) was evaporated to dryness under reduced pressure, and the residue was dried *in vacuo* for two minutes. $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ (0.51g, 1.21mmol) was added and the reaction vessel was cooled to -78°. Benzene (10ml) was added slowly. The solid was allowed to warm to room temperature and melt to a deep green solution. The solution was stirred at room temperature for 2h, when it slowly turned deep yellow-brown. The suspension was cooled to -78° and methanol (0.5ml) was added dropwise. The solid was allowed to melt and the yellow-brown suspension was evaporated to dryness under reduced pressure. The residue was extracted with benzene and the benzene extract was evaporated to dryness under reduced pressure, leaving a viscous dark brown oil. Sublimation of the oil at $100°/10^{-5}$mm Hg onto a cold finger at -20° gave a yellow-green solid. Sublimation of the solid yielded the product as a fine yellow, very air-sensitive powder (79mg). The product contained $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ (0.14mmol, 12%), $RuHBr(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ (22μmol, 2%) and $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ (9μmol, 0.7%), as shown by ^1H NMR spectroscopy.

$RuHCl(\eta^6\text{-}C_6Me_6)(PMe_3)$ was treated similarly. On methanolysis, the orange yellow reaction mixture rapidly turned into a deep violet suspension. The suspension was evaporated to dryness under reduced pressure, leaving a red-brown oil. Repeated recrystallization from toluene/n-hexane and filtration through filter-aid only precipitated a brown flocculent material. The filtrate was evaporated to dryness and the residue was slowly sublimed at $55°/2x10^{-6}$mm Hg onto a cold finger cooled to -20°, depositing $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PMe_3)$ [53] as a very air-sensitive yellow powder in approximately 8% yield. This was

contaminated with 12 to 25% free hexamethylbenzene.

Similar treatment of $RuHCl(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$ (0.50 g, 1.41mmol) with phenyllithium gave, on methanolysis, a black solution with a violet precipitate. This was evaporated to dryness under reduced pressure. The residue was extracted with benzene and the benzene extract was reduced in volume to approximately 5ml. The extract was then loaded onto an alumina column and was eluted with benzene. The first band to elute was yellow in colour and was evaporated to dryness under reduced pressure. (The remaining bands to elute were discarded, as they were found to contain only by-products.) Recrystallization from n-hexane by cooling to -78° afforded a sticky yellow microcrystalline solid (31mg), which, on the basis of NMR, IR and mass spectroscopy, is probably the complex $Ru(C_6H_5)_2(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$ [52]. Further attempts to isolate $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$ [51] were unsuccessful.

6) Preparation of $\overline{RuH(o\text{-}CH_2C_6H_4PPh_2)(\eta^6\text{-}C_6Me_6)}$ [38] from $\overline{RuCl(o\text{-}CH_2C_6H_4PPh_2)(\eta^6\text{-}C_6Me_6)}$ [26]

A suspension of $\overline{RuCl(\underline{o}\text{-}CH_2C_6H_4PPh_2)(\eta^6\text{-}C_6Me_6)}$ [26] (0.50g, 0.87mmol) and sodium borohydride (0.64g, 17mmol) in 2-propanol (50ml) was heated to reflux for 40h. The yellow suspension was cooled and evaporated to dryness under reduced pressure. The residue was extracted with toluene and the extract was evaporated to small volume under reduced pressure. Fine yellow crystals of [38] (0.23g, 0.43mmol, 49%) were precipitated by the addition of n-hexane.

Table 3-6 : Analytical Data for Cyclometallated and Hydridophenyl Complexes

Calculated figures in parentheses.

Compound	MW[a]	C	H	P
[27] $Ru\overline{H(\underline{o}\text{-}C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$	526	68.74 (68.55)	6.51 (6.33)	6.17 (5.89)
[29] $Ru\overline{H([\underline{o}\text{-}C_6H_3\text{-}\underline{p}\text{-}F]P[\underline{p}\text{-}C_6H_4F]_2)}(\eta^6\text{-}C_6Me_6)$[b]	580	61.67 (62.17)	5.27 (5.22)	5.97 (5.34)
[30] $Ru\overline{H([\underline{o}\text{-}C_6H_3\text{-}\underline{p}\text{-}CH_3]P[\underline{p}\text{-}C_6H_4CH_3]_2)}(\eta^6\text{-}C_6Me_6)$	568	69.21 (69.82)	6.93 (6.92)	5.57 (5.46)
[31] $Ru\overline{H(CH_2CMe_2PPh_2)}(\eta^6\text{-}C_6Me_6)$	506	67.05 (66.51)	7.79 (7.38)	5.86 (6.13)
[32] $Ru\overline{H(\underline{o}\text{-}C_6H_4PBu^tPh)}(\eta^6\text{-}C_6Me_6)$	506	67.13 (66.51)	7.58 (7.38)	5.90 (6.13)
[33] $Ru\overline{H(CH_2CHMePPh_2)}(\eta^6\text{-}C_6Me_6)$	492	65.74 (65.97)	7.68 (7.18)	6.09 (6.30)
[34] $Ru\overline{H(\underline{o}\text{-}C_6H_4PPhPr^i)}(\eta^6\text{-}C_6Me_6)$	492	66.11 (65.97)	7.26 (7.18)	6.23 (6.30)
[36] $Ru\overline{H(\underline{o}\text{-}C_6H_4PEtPh)}(\eta^6\text{-}C_6Me_6)$	478	64.95 (65.39)	6.99 (6.96)	6.48 (6.49)
[38] $Ru\overline{H(\underline{o}\text{-}CH_2C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$	540	68.66[c] (69.00) 68.23[d] (69.00)	6.46[c] (6.54) 6.74[d] (6.54)	5.50[c] (5.74) 5.34[d] (5.74)
[39] $Ru\overline{H(\underline{o}\text{-}C_6H_4PPhPr^n)}(\eta^6\text{-}C_6Me_6)$	492	65.97 (65.97)	7.76 (7.18)	6.80 (6.30)
[40] $Ru\overline{H(CH_2CH_2CH_2PPh_2)}(\eta^6\text{-}C_6Me_6)$	492	66.59 (65.97)	7.41 (7.18)	6.06 (6.30)
[42] $Ru\overline{H(CH_2CMe_2PBu^tMe)}(\eta^6\text{-}C_6Me_6)$	424	59.64 (59.55)	9.59 (9.82)	7.12 (7.31)

Table 3-6 : Analytical Data for Cyclometallated and Hydridophenyl Complexes (Cont'd)

Compound	MW[a]	C	H	P
[43] $R\overline{uH(CH_2CMe_2}PBu^tEt)(\eta^6\text{-}C_6Me_6)$	438	62.75 (60.38)	9.83 (9.44)	7.98 (7.08)
		58.93[e] (60.38)	8.39[e] (9.44)	7.14[e] (7.08)
[45] $R\overline{uH(CH_2CMe_2}PBu^tPr^n)(\eta^6\text{-}C_6Me_6)$[f]	452	61.37 (61.17)	10.26 (9.60)	6.78 (6.86)
[46] $R\overline{uH(CH_2CH_2CH_2}PBu^t_2)(\eta^6\text{-}C_6Me_6)$[f]				
[47] $R\overline{uH(CH_2CHMe}PPr^i_2)(\eta^6\text{-}C_6Me_6)$	424	59.75 (59.55)	9.52 (9.28)	7.43 (7.31)
[48] $R\overline{uH(CH_2CMe_2}PMe_2)(\eta^6\text{-}C_6Me_6)$[g]	382	56.65 (56.67)	8.87 (8.72)	
[49] $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$		62.21[h] (62.72)	8.61[h] (8.55)	6.24[h] (6.74)
		62.04[i] (62.72)	9.06[i] (8.55)	7.59[i] (6.74)
[53] $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PMe_3).0.13(C_6Me_6)$[j]		61.78 (61.78)	8.45 (8.12)	7.06 (6.89)

a: Parent ion (^{102}Ru) in 70eV mass spectrum.

b: F 9.23 (9.83)

c: Prepared from $R\overline{uCl(o\text{-}CH_2C_6H_4}PPh_2)(\eta^6\text{-}C_6Me_6)$.

d: Prepared from $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_2o\text{-}Tol)$.

e: Repeat analysis on an independent sample.

f: Mixture of [45] and [46].

g: Contains 30% $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$. Parent ion for $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ also present at m/z = 384.

h: Prepared from $RuHCl(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$.

i: Prepared from $R\overline{uH(CH_2CMe_2}PMe_2)(\eta^6\text{-}C_6Me_6)$ [48].

j: Contains free C_6Me_6.

7) Isomerization and Reaction Kinetics

Samples were usually prepared by sealing a solution of the species being studied (50 to 100mg) in the appropriate solvent (2.4 to 3.2ml) in vacuo in a 10mm NMR tube. The sample for monitoring the reaction of [48] with benzene was prepared by sealing [48] in benzene (0.7ml) in a 5mm NMR tube concentric with a 10mm NMR tube containing D_2O as NMR locking solvent. $^{31}P[^1H]$ NMR spectroscopy was used to monitor the reaction kinetics. Spectra were acquired for 30min, with a pulse repetition rate of 1.0s; eight to ten spectra were acquired in a 16h period. Integrals measuring peak area were used to determine the relative quantities of the species present. Reaction rates were determined from a least squares fit, and the rate constants calculated by using the appropriate model for the reaction.[157] The errors quoted are 90% confidence limits.[30] All calculations were performed using the least squares program "LSTSQR" on the Research School of Chemistry computer. Estimates of the activation energy were made using the formula $\Delta G^{\ddagger} = -RT \ln(hk/k_B T)$ {k_B = Boltzmann's constant, k = reaction rate}. The following instrumental conditions were used:

Table 3-7: Experimental Conditions for Kinetics Experiments

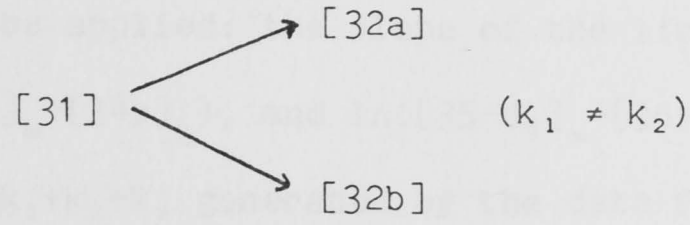
Reaction	Solvent	T (°C)	Sweep Width (Hz)	Acquisition Time (s)
[31] ⟶ [32]	C_6D_6	50	5000	0.8192
	THF-d_8	50	5000	0.8192
[33] ⟶ [34] + [35-d_6]	C_6D_6	20	10000	0.8192
[39] ⟶ [40]	1:2 C_6D_{12}/ C_6H_{12}	60	13900	0.5898
[48] + C_6D_6 ⟶ [49-d_6]	C_6D_6	35	12000	0.6881
[48] + C_6H_6 ⟶ [49]	C_6H_6/D_2O	35	12000	0.6881

For details on how the spectroscopic data were used to determine the relative quantities of species present, see Appendix 2, p185.

a) Isomerization of $\overbrace{RuH(CH_2CMe_2PPh_2)}(\eta^6\text{-}C_6Me_6)$ [31]

There was no observable NOE difference between the ^{31}P resonances of [31] and [32] at 50°. The difference in T_1's would result in a 3% error in the measurement of peak areas under the experimental conditions.

The model used for this reaction was:



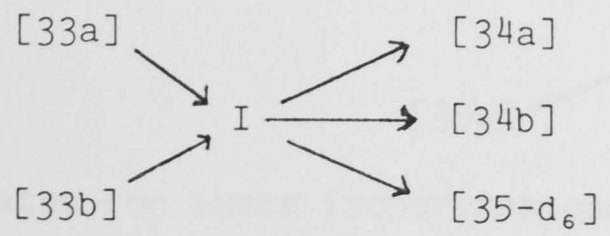
The slope of the lines formed by $\ln([31]_o\text{-}[31]_t)$, $\ln([32a]_\infty\text{-}[32a]_t)$ and $\ln([32b]_\infty\text{-}[32b]_t)$ have slope $-(k_1+k_2)$, the rate of consumption of A. A plot of $[32a]_t$ and $[32b]_t$ against $([31]_o\text{-}[31]_t)$ gives lines with slopes $k_1/(k_1+k_2)$ and $k_2/(k_1+k_2)$ respectively.[157] The value of (k_1+k_2) generated by the data for [32a] were used, as it was the most reliable.

b) Isomerization of $\overbrace{RuH(CH_2CHMePPh_2)}(\eta^6\text{-}C_6Me_6)$ [33]

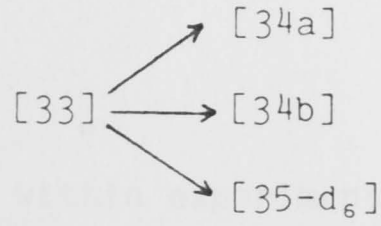
The analysis of the data for the reaction [33] $\longrightarrow$ [34] + [35-d_6] was complicated by the fact that the species [35-d_6] was outside the frequency domain observed during the acquisition of kinetic data, but it was observed in a subsequent spectrum. Data were derived for [35-d_6] by difference, using Ph_3PO which had been added as an internal standard. Thus the data for [35-d_6] are not very reliable. There were no significant T_1 or NOE differences between the ^{31}P resonances of [33], [34] or [35-d_6] under the experimental conditions.

The appropriate model for this reaction is (I), but as [33a] and [33b] were consumed at equal rates within experimental error, the rates of formation of [34a], [34b] and [35-d_6] were calculated using

model (II). Methodology similar to that for the



(I)



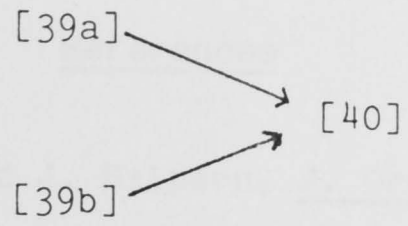
(II)

isomerization of [31] can be applied: the slope of the lines formed by $\ln([34a]_\infty-[34a]_t)$, $\ln([34b]_\infty-[34b]_t)$, and $\ln([35\text{-}d_6]_\infty-[35\text{-}d_6]_t)$ is $-(k_1+k_2+k_3)$. The value of $k_1+k_2+k_3$ generated by the data for [34a] was used. Plots of $([34a]_t-[34a]_o)$, $([34b]_t-[34b]_o)$ and $([35\text{-}d_6]_t-[35\text{-}d_6]_o)$ against $([33]_o-[33]_t)$ give $k_1/(k_1+k_2+k_3)$, $k_2/(k_1+k_2+k_3)$ and $k_3/(k_1+k_2+k_3)$ respectively.

c) Isomerization of $\overline{RuH(o\text{-}C_6H_4PPhPr^n}$)($\eta^6$-$C_6Me_6$) [39]

The analysis of the data for the reaction [39] ⟶ [40] was complicated by several factors: (i) The sample used to follow the isomerization was significantly contaminated, and the concentration of the impurities varied during the course of the experiment; (ii) There was a significant NOE difference between the ^{31}P resonances of [39a] and [40] under the experimental conditions. The impurities were ignored and the raw data for [39a] and [40] were multiplied by the appropriate values to compensate for NOE differences. As a consequence, the results from this experiment must be treated as being only indicative of the true rates of reaction. There was no significant difference in T_1 between species [39] and [40].

The model adopted for this reaction was:



As the rates for these isomerizations were equal within experimental error, no further calculations were required.[157]

d) Reaction of $\overline{RuH(CH_2CMe_2PMe_2)}(\eta^6\text{-}C_6Me_6)$ with benzene and benzene-d_6

The data for the reactions [48] + C_6H_6 ⟶ [49] and [48] + C_6D_6 ⟶ [49-d_6] were analyzed by following the relative concentration of each species using $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$ as an internal standard. This approach was taken as there were significant T_1 and NOE differences between the ^{31}P resonances of species [49], [49-d_6] and [48]. This approach was possible because there were no side reactions, and the reaction was complete during the acquisition of the kinetic data. The model adopted was a simple (pseudo) first order model, [48] ⟶ [49].

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Appendix

List of Compound Numbers.

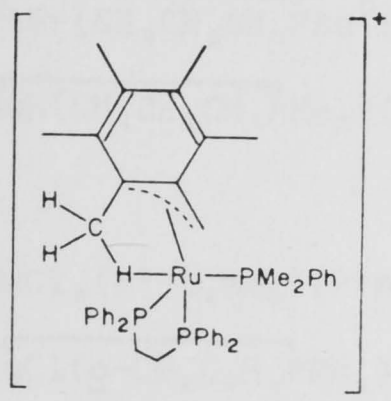
* [Na] refers to the major diastereoisomer of N, [Nb] to the minor.

[1] $RuCl_2(\eta^6\text{-}C_6H_6)(PMePh_2)$

[2] $\{[Ru(\eta^6\text{-}C_6Me_6)]_2(\mu\text{-}H_2)(\mu\text{-}Cl)\}Cl$

[3] $Ru[\eta^4\text{-}\underline{o}\text{-}C_6(CH_2)_2Me_4](PR_3)_2(PR'_3)$

[4]



[5] $Ru[\eta^4\text{-}\underline{o}\text{-}C_6(CH_2)_2Me_4](\eta^6\text{-}C_6Me_6)$

[6] $[Ru(\eta^5\text{-}C_6H_5CH_2)(\eta^6\text{-}C_6Me_6)]^+$

[7] $\overbrace{RuH[(\underline{o}\text{-}C_6H_3\text{-}\underline{p}\text{-}X)PAr_2}](\eta^6\text{-}C_6Me_6)$

[8] $Ru(\eta^6\text{-}C_6Me_6)(\eta^2\text{-}C_2H_4)L$

[9] $\overbrace{RuH(CH_2CHMePPr^i_2}](\eta^6\text{-}C_6H_6)$

[10] $RuH(C_6H_5)(\eta^6\text{-}C_6H_6)(PPr^i_3)$

[11] $\{[Lu(\eta^5\text{-}C_5Me_5)_2]_2(\mu\text{-}\underline{p}\text{-}C_6H_4)\}$

[12] $IrH_2(\eta^5\text{-}C_5Me_5)(PMe_3)$

[13] $RhH_2(\eta^5\text{-}C_5Me_5)(PMe_3)$

[14] $\overbrace{IrH(CH_2SiMe_2CH_2}](PMe_3)_3$

[15] $\underline{fac}\text{-}[\overbrace{IrH(\underline{o}\text{-}C_6H_4PMe_2}](PMe_2Ph)_3]^+$

[16] $\overbrace{IrHCl(\underline{o}\text{-}C_6H_4PPh_2)}(PPh_3)_2$

[17] $\underline{fac}\text{-}\overbrace{FeH(CH_2PMe_2)}(PMe_3)_3$

[18] $Ru(CH_3)(\eta^5\text{-}C_5H_5)(PPh_3)_2$

[19] $\overbrace{Ru(\underline{o}\text{-}C_6H_4PPh_2)}(\eta^5\text{-}C_5H_5)(PPh_3)$

[20] $\overbrace{Pt(CHEtPPr^n_2)}(Carb)(PPr^n_3)$

[21] $\overbrace{IrCl_2(CH_2PMeR)}(PMe_2R)_2$ (R = Me, Ph)

[22] $\overbrace{PdCl(CH_2CMe_2PBu^t_2)}(PBu^t_3)$

[23] $\overbrace{PtBr(CH_2CH_2CH_2PBu^tPr^n)}(PBu^tPr^n_2)$

[24] $\overbrace{RhH(CH_2CH_2CH_2PMe_2)}(\eta^5\text{-}C_5Me_5)$

[25] $RuCl_2(\eta^6\text{-}C_6Me_6)(PPh_2\underline{o}\text{-}Tol)$

[26] $\overbrace{RuCl(\underline{o}\text{-}CH_2C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$

[27] $\overbrace{RuH(\underline{o}\text{-}C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$

[28] $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PPh_3)$

[29] $\overbrace{RuH([\underline{o}\text{-}C_6H_3\text{-}\underline{p}\text{-}F]P[\underline{p}\text{-}C_6H_4F]_2)}(\eta^6\text{-}C_6Me_6)$

[30] $\overbrace{RuH([\underline{o}\text{-}C_6H_3\text{-}\underline{p}\text{-}CH_3]P[\underline{p}\text{-}C_6H_4CH_3]_2)}(\eta^6\text{-}C_6Me_6)$

[31] $\overbrace{RuH(CH_2CMe_2PPh_2)}(\eta^6\text{-}C_6Me_6)$

[32]* $\overbrace{RuH(\underline{o}\text{-}C_6H_4PBu^tPh)}(\eta^6\text{-}C_6Me_6)$

[33]* $\overbrace{RuH(CH_2CHMePPh_2)}(\eta^6\text{-}C_6Me_6)$

[34]* $\overbrace{RuH(\underline{o}\text{-}C_6H_4PPhPr^i)}(\eta^6\text{-}C_6Me_6)$

[35-d_6] $RuD(C_6D_5)(\eta^6\text{-}C_6Me_6)(PPh_2Pr^i)$

[36]* $\overbrace{RuH(\underline{o}\text{-}C_6H_4PEtPh)}(\eta^6\text{-}C_6Me_6)$

[37] $\overbrace{RuH(\underline{o}\text{-}C_6H_4PPh\{\underline{o}\text{-}Tol\})}(\eta^6\text{-}C_6Me_6)$

[38] $\overbrace{RuH(\underline{o}\text{-}CH_2C_6H_4PPh_2)}(\eta^6\text{-}C_6Me_6)$

[39]* $Ru\overline{H(\underline{o}\text{-}C_6H_4PPhPr^n)}(\eta^6\text{-}C_6Me_6)$

[40] $Ru\overline{H(CH_2CH_2CH_2PPh_2)}(\eta^6\text{-}C_6Me_6)$

[41] $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PPh_2Pr^n)$

[42] $Ru\overline{H(CH_2CMe_2PBu^tMe)}(\eta^6\text{-}C_6Me_6)$

[43]* $Ru\overline{H(CH_2CMe_2PBu^tEt)}(\eta^6\text{-}C_6Me_6)$

[44] $Ru\overline{H(CH_2CH_2PBu^t_2)}(\eta^6\text{-}C_6Me_6)$

[45]* $Ru\overline{H(CH_2CMe_2PBu^tPr^n)}(\eta^6\text{-}C_6Me_6)$

[46] $Ru\overline{H(CH_2CH_2CH_2PBu^t_2)}(\eta^6\text{-}C_6Me_6)$

[47]* $Ru\overline{H(CH_2CHMePPr^i_2)}(\eta^6\text{-}C_6Me_6)$

[48] $Ru\overline{H(CH_2CMe_2PMe_2)}(\eta^6\text{-}C_6Me_6)$

[49] $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$

[50]* $Ru\overline{H(\underline{o}\text{-}C_6H_4PMePh)}(\eta^6\text{-}C_6Me_6)$

[51] $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$

[52] $Ru(C_6H_5)_2(\eta^6\text{-}C_6Me_6)(PMe_2Ph)$

[53] $RuH(C_6H_5)(\eta^6\text{-}C_6Me_6)(PMe_3)$

[54] $[Pt\overline{(\underline{o}\text{-}CH_2OC_6H_4PPh_2)}(\mu\text{-}Cl)]_2$

[55] $Pt\overline{(\underline{o}\text{-}OC_6H_4PPh_2)}_2$

[56] $Ir\overline{H(\underline{o}\text{-}C_6H_4PPh_2)}(\eta^5\text{-}C_5H_5)$

[57] $IrH(C_6H_5)(\eta^5\text{-}C_5H_5)(PPh_3)$

[58] $\underline{mer}\text{-}RuH(\eta^2\text{-}BH_4)(PMe_3)_3$

[59] $IrHMe(\eta^5\text{-}C_5Me_5)(PMe_3)$

APPENDIX 2

Additional Details of Data Analysis for Isomerization Reactions and Explanation of Symbols in Figures {see pp. 74, 80, 97, 120 and 170}.

a) Isomerization of $RuH(CH_2CMe_2PPh_2)(\eta^6\text{-}C_6Me_6)$ [31].

The integral of peak areas for peaks at δ 28.0, 13.4 and 7.6ppm, due to [31], [32a] and [32b] respectively, were summed for each spectrum. The intensity of each peak integral was then divided by the sum of the peak areas for each spectrum. This is the mole fraction, X_i, of the species [31], [32a] and [32b]. The least squares analysis was performed using the natural logarithm of the mole fraction of [31], and the natural logarithm of the difference between $X_{[32a]}$ at t_∞ and $X_{[32a]}$ at time t; similarly for [32b]. The least squares program LSTSQR gave k as the "N2 computed parameter" and the standard error as "external errors". The 90% confidence limits were obtained by multiplying the standard error by the appropriate factor from t-tables at 5% significance.[30] The rate constants were calculated as outlined in the experimental section {p170}.

The discrepancy with literature results arises from use of the incorrect formula $\ln(1-X_{[32]})$ in place of $\ln(X_{[32]\infty}-X_{[32]_0})$ in reference 14.

b) Isomerization of $RuH(CH_2CHMePPh_2)(\eta^6\text{-}C_6Me_6)$ [33].

The ratio of ([33]+[34])/Ph_3PO was initially 2.0 on a molar basis. However, the observed ratio of peak areas was approximately 3.05, presumably due to relaxation time differences between the complexes and Ph_3PO. The variation from 3.05 as the reaction proceeded was assumed to be due to the formation of $RuD(C_6D_5)(\eta^6\text{-}C_6Me_6)(PPh_2Pr^i)$, [35-$d_6$]. This was used to derive the data for

[35-d_6]. The mole fractions of [33a], [33b], [34a], [34b] and [35-d_6] were calculated in a similar manner to the above example. Rate constants were derived as outlined in the experimental section {p170}.

c) Isomerization of $\overbrace{RuH(o\text{-}C_6H_4PPhPr^n}$)($\eta^6$-$C_6Me_6$) [39].

As noted on p97 and in the experimental section {p171}, the impurity peaks in this experiment were ignored. The NOE test spectra {see section e) of this Appendix} showed that there were significant differences in NOE between species [39a] and [40] under the experimental conditions. The discrepancy for [39b] was within experimental error and was ignored. The NOE test spectra showed that the mole fraction of [39a] was overestimated by 19%, whilst the mole fraction of [40] was underestimated by 9%. The integrals of peak areas of [39a] were divided by 1.19 and those of [40] multiplied by 1.09 prior to further analysis of the data. The data were handled in a similar manner to that for [31], using the model described on p171.

d) Reaction of $\overbrace{RuH(CH_2CMe_2PMe_2}$)($\eta^6$-$C_6Me_6$) [48] with benzene and with benzene-d_6.

From integrals of peak areas, it was apparent that there were significant T_1 or NOE differences between [48], [49] and $RuH_2(\eta^6\text{-}C_6Me_6)(PBu^tMe_2)$. The dihydride complex was assumed to be unreactive and was used as an internal standard. The dihydride was present as 25% of the sample based on the integration of the hydride resonances in a ^1H NMR spectrum. At the end of the reaction, no [48] remained. Thus the ratio of peak areas [49]/dihydride in the $^{31}P[^1H]$ NMR spectrum should be 3.0, but was observed to be 4.0 = $([49]/dihydride)_\infty$. At time t, $([49]/dihydride)_t/([49]/dihydride)_\infty = X_{[49]}$, the mole fraction of [49]. For the first spectrum only, this was used to calculate $X_{[48]}$ {= $1-X_{[49]}$}, the mole fraction of [48]. The ratio $([48]/dihydride)_0$

{at t = 0} was calculated using the data for the first spectrum: $([48]/\text{dihydride})_0 = ([48]/\text{dihydride})/X_{[48]} = 3.53$. At time t, $X_{[48]}$ was calculated using $X_{[48]} = ([48]/\text{dihydride})_t/([48]/\text{dihydride})_0$. The least squares analysis was performed on $\ln X_{[48]}$ and $\ln(1 - X_{[49]})$ to determine independently the rate of reaction of [48] and the rate of formation of [49].

e) T_1 and NOE Test Spectra

Tests for T_1 and NOE differences between species present in the isomerization reactions of [31], [33] and [39] were made by obtaining the following series of ^{31}P NMR spectra one immediately after the other under the experimental conditions shown in Table 3-7 on a sample containing approximately equal amounts of the kinetic and thermodynamic products:

(1) ^1H decoupled, pulse repetition rate 1.0s;

(2) ^1H decoupled, pulse repetition rate 10.0s;

(3) ^1H decoupled, pulse repetition rate 1.0s;

(4) ^1H coupled, pulse repetition rate 1.0s;

(5) ^1H decoupled, pulse repetition rate 1.0s.

Spectra (1), (3) and (5) were obtained under precisely the same conditions as those used for the isomerization experiments. The conditions under which spectrum (2) was obtained should allow for complete relaxation of the phosphorus nuclei, whereas there should be no NOE contribution to peak intensities under the conditions of spectrum (4). Assuming first order {or in the the case of [35-d_6], pseudo-first order} behaviour, if $\ln X_{(2)} = [\ln X_{(1)} + \ln X_{(3)}]/2$ for each peak, then there is no significant difference in T_1 between the species, and similarly, if $\ln X_{(4)} = [\ln X_{(3)} + \ln X_{(5)}]/2$ for each peak, then there is no significant NOE difference between the species under the experimental conditions. Here, $X_{(n)}$ is the mole fraction for

a particular species in spectrum (n), as defined in the preceding sections of this Appendix.

f) Explanation of Symbols in Figures 3-6, 3-8, 3-9 and 3-16.

For Figures 3-6, 3-8, 3-9, $X_n = Area_n/Area_{total}$. For precise derivation, see above.

Figure 3-6, p75.

$X_{[31]}$ mole fraction of [31].

$X_{[31]_o}$ mole fraction of [31] at t=0.

$X_{[32]}$ mole fraction of [32].

$X_{[32]_\infty}$ mole fraction of [32] at t=∞.

Figure 3-8, p81.

$X_{[33]}$ mole fraction of [33a] or [33b].

$X_{[33]_o}$ mole fraction of [33a] or [33b] for the first spectrum {t = 0.7h} was used, as the system did display first order behaviour, and it was most convenient to use these values.

$X_{[34]}$ mole fraction of [34a] or [34b].

$X_{[34]_o}$ mole fraction of [34a] or [34b] at t = 0.7h, see above.

$X_{[34]_\infty}$ mole fraction of [34a] or [34b] at t=∞.

$X_{[35\text{-}d_6]}$ mole fraction of [35-d_6].

$X_{[35\text{-}d_6]_o}$ mole fraction of [35-d_6] at t = 0.7h, see above.

$X_{[35\text{-}d_6]_\infty}$ mole fraction of [35-d_6] at t=∞.

Figure 3-9, p98.

$X_{[39]}$ mole fraction of [39a] or [39b].

$X_{[40]}$ mole fraction of [40].

Figure 3-16, p121.

$[48]/[48]_0$ mole fraction of [48].

$[49]/[49]_\infty$ mole fraction of [49].

$[49\text{-}d_6]/[49\text{-}d_6]_\infty$ mole fraction of $[49\text{-}d_6]$.